THE TECHNOLOGY OF NATURAL RESINS

The Technology of Natural Resins

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PREFACE

Although an extensive literature exists on the synthetic resins, a corresponding development of the much older field of the natural materials is lacking. Volumes specifically devoted to shellac and rosin are in existence, but there is a decided gap in our technical literature concerning the important damar, copal, East India, and related resins from the viewpoint of their properties, their applications, industrial uses, development, and technology. This volume is an attempt to fill the gap.

Many of the earlier scientific articles dealing with natural resin compositions are conflicting and confusing. This is particularly so in that work was done on individual samples of botanical or of indefinite origin and did not concern itself with the commercial graded materials, the annual consumption of which in the United States is of the order of 40 to 50 million pounds.

Recognizing the desirability and necessity of obtaining fundamental information on the products they were distributing, the American Gum Importers Association, an organization of those firms in the natural resin business in the United States, embarked as their major activity on a research program at the laboratories of the Hilton Davis Company in Cincinnati at the end of 1932. Shortly afterward the Nederlandsch Indische Vereeniging voor den Handel in Gommen, an organization comprising the shippers and exporters of the resins in the Netherlands Indies, also organized a development program at the same laboratories, which program was specifically directed to the resins of Dutch origin. These constitute by far the major portion of the world production and the United States consumption. About a year later, the American Gum Importers Association and then the Nederlandsch Indische Vereeniging voor den Handel in Gommen asked the senior author of this volume to direct the development and research activities. In the fall of 1936, the senior author designed laboratories in Brooklyn for the work of the two organizations cooperating under a single directing head. The publications resulting from the work constitute the major sources of information on the natural resins. In 1940 separate laboratories were estab-

lished by the Netherlands Indies group to intensify the work on resin processing.

In the conduct of the work and in the preparation of this volume, the authors have had the cooperation of the Laboratorium voor Scheikundig Onderzoek at Batavia, Java; Dr. D. R. Koolhaas, director of the Laboratory and now in the Department of Economic Affairs; Mr. C. van de Koppel, formerly chief forester, Netherlands East Indies; Mr. E. C. Zimmerman, Netherlands Indies Trade Commissioner for the United States, and many others to whom specific acknowledgment is made at various points in the text.

Emphasis in the volume has been placed upon the technology of the resins, their industrial formulations, the properties of the resins and their combinations with other materials, and their place in commerce. The treatment is more practical than theoretical or even scientific. From the viewpoint of terminology, shellac and rosin are excluded. It is hoped that this volume will provide a technical background for the important commercial resins of natural origin. The authors will welcome comments and criticisms at all times.

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Munsey Park,
Manhasset, N. Y.
January, 1942.

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CHAPTER I

INTRODUCTION

The collection, grading, sorting, distribution, preparation for marketing, warehousing, and the commerce of the natural resins is a coordinated and systematic business, worldwide in its ramifications, connections, and operations. The business is as old as the varnish art and practice itself. In its early stages it was conducted with much secrecy, confusion of names, and generally with an aura of mystery. The collectors of resin knew that there was a demand for the product but had little, if any, knowledge as to the required specifications or the actual applications. The distributors in turn seldom knew much of the operations of their customers, so that the distributors served merely as traders who were unable to provide information about their products to further the use thereof. Designations which hid the identity of the resin, or else a multiplicity of names for the same article, coupled with sorting of resins to satisfy individual idiosyncrasies of purchasers added to the confusion. Such, however, is now a matter of the past.

The natural resins are exudations of trees of many different genera and species. These exudations or secretions may be those of living trees, an example of which is damar, or may be the fossilized product of trees long dead, as congo or kauri. The products of different species appear on the market as different resins, each with a different set of properties. From the botanical and forest viewpoint, the trees and their resins have been thoroughly and competently studied over long time periods. This is especially true in the Netherlands Indies where governmental departments have devoted their energy continuously to the economic botanical aspects. The natural resins resulting from trees which themselves are capable of infinite renewal and increase, are not subject to vanishing supplies of raw materials but may be expected to meet all demands.

From the viewpoint of terminology of this book, rosin and shellac are not included within the term "natural resins," although it is apparent that this is an artificial classification.

The trade usually refers to the natural resins as "gums." This is distinctly a misnomer, as in strict terminology the gums are related to the sugars and the carbohydrates. The gums are soluble in water, form-

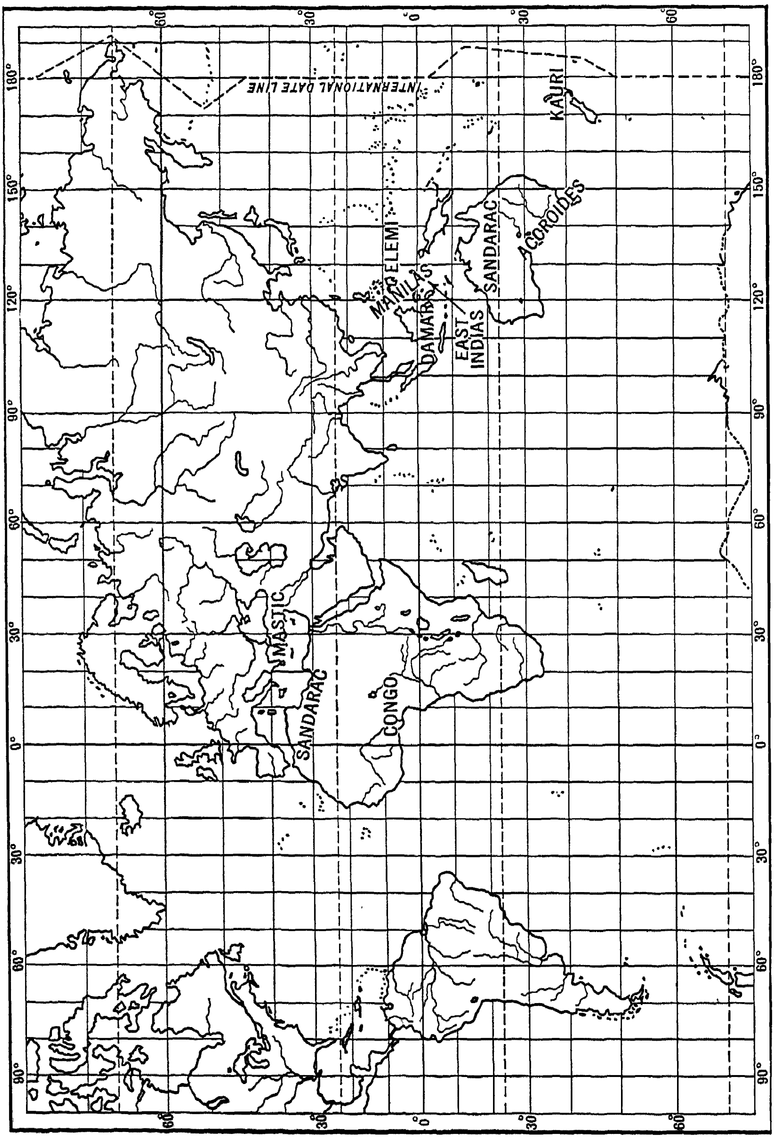
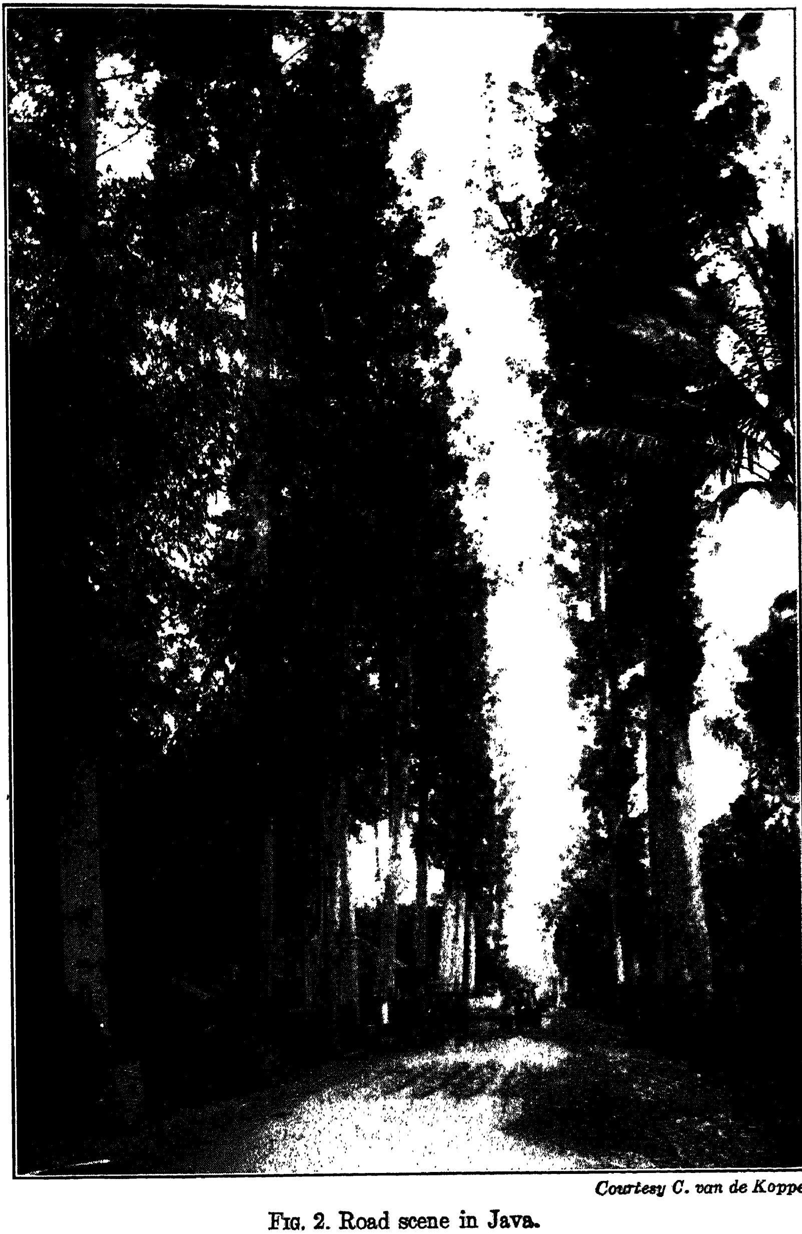


FIG. 1. Sources of natural resins.



Courtesy C. van de Koppel

Fig. 2. Road scene in Java.

ing viscous solutions, and they are insoluble in drying oils and organic solvents. On heating, they decompose completely without melting, usually showing charring. In contradistinction, the resins discussed in this

Courtesy C. van de Koppel

FIG. 3. Javanese resin collectors.

volume are insoluble in water. They show more or less solution in organic solvents and vegetable oils. They are chemically related to the terpenes or the essential oils. When heated, the resins melt with distillation of volatile oils as the temperature is increased. They do not

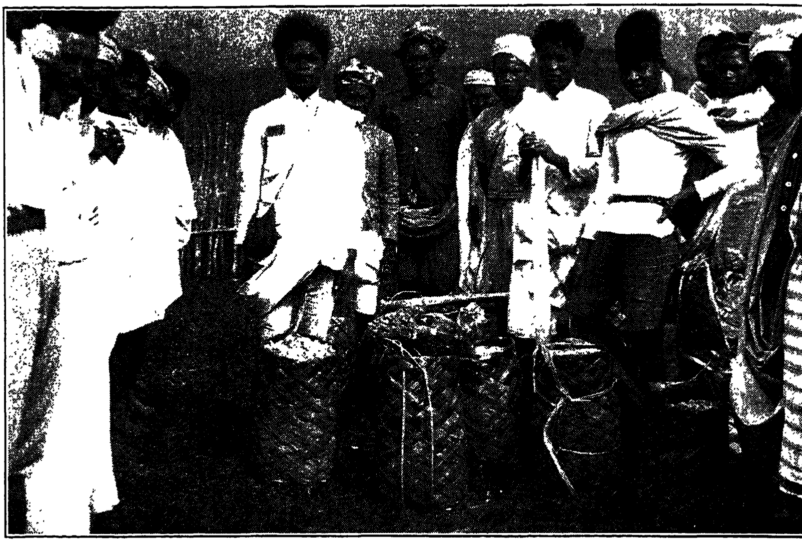
show a "carbonizing point," nor do they produce coke when destructively distilled. By thermal processing, the resins may be converted into "run" gum or resin which is soluble in hot vegetable oils, the resulting combination being a varnish base. Some of the softer resins are directly soluble in solvents or in oils, but in all cases are totally insoluble in water. The major uses of the natural resins are in finishing compositions, inks, lacquers, linoleums, varnishes, paints, plastics, sizes, polishes, and coating compositions. The true gums, on the other hand, find their major applications in adhesives, sizes, and to some

Courtesy C. van de Koppel

FIG. 4. Native resin collectors carrying their load from the mountains to Lenke, on Lake Towoeti, Celebes. Each basket contains about 140 pounds of resin.

extent in food products. Examples of these true gums are arabic, tragacanth, karaya, locust-seed and the like. The resins are totally unrelated to the gums either physically, chemically, or applicationwise.

The resins are divided from the point of use into two major classes: first, those which are spirit soluble, and second, those which are oil soluble. The term spirit originally referred to alcohol, but now embraces a large variety of solvents. The spirit-soluble resins are generally put into solution directly by mechanical mixing or agitation or standing in contact. The oil-soluble type needs to be fused or processed by thermal methods to make it soluble. The operation is referred to as "running" by the varnish maker. In general, the spirit-soluble resins, an example of which are the manilas, are of the soft variety, whereas the oil-soluble type is usually hard. The resins are known under names which are indicative either of their source of origin, or of a distinguish-



Courtesy C. van de Koppel

Fig. 5. Resin collectors in the field.

Courtesy C. van de Koppel

FIG. 6. Papuan resin collectors at a trading post.

ing characteristic of the resin, or its color, or of the port at which they enter commerce. They may be classified into four major types: the damars which include those known under this name; the east indias (originating in the Netherlands Indies) which are semi-fossil damars; the copals, including the manilas with their wide range of hardnesses, from the soft melengkets through stages of hardness and fossilization to the hard boea, as well as the congos which are the hardest of all the commercial materials, and the kauris; and a fourth group which are in

Courtesy C. van de Koppel

FIG. 7. Sorting East India resins.

a miscellaneous class including the balsam-like elemi, accroides, mastic, and sandarac. There is practically a continuous series as regards solubility and hardness, from the fresh tappings of living trees represented by the softest damars, to the hardest copals of the fossil type centuries old. The classification of the resins employed in this book is given in Table I. The individual resins are discussed separately, with details of their origin, collection, and other factors. Figure 1 is a map showing the areas of the earth from which the commercial quantities of these resins arise. In general they originate in the Congo district of Africa and adjoining territory from which the resin is named; New Zealand which produces kauris; the Netherlands Indies, particularly Java, the East Indies, and other islands, the source of damar; the manilas, sometimes called macassars, from Celebes, Malaya, the Philippine Islands which produce manila and elemi, and adjacent territories. They are

obtained from definite species and from groups of trees in a systematic manner, generally under governmental supervision. In Figs. 2 to 7 are shown a road scene in Java, Javanese resin collectors, porters carrying resin in the bush in the Celebes and in the fields, a trading post in Papua, and a sorting station.

TABLE I

CLASSIFICATION OF NATURAL RESINS

1. Damars: low acid number resins of recent origin, solvent and oil soluble
   A. Batavia
   B. Singapore
2. East Indias: semi-fossil or semi-recent resins related to the damars, solvent and oil soluble
   A. Batu
   B. Black
   C. Pale east india Singapore (rasak)
   D. Pale east india Macassar (hiroe)
3. Copals: in general, higher acid numbers than damars
   A. Manila
      1. Melengket or soft resins of recent origin, spirit soluble
      2. Loba or half-hard of semi-recent origin, spirit soluble
      3. Philippine manilas (almaciga) of semi-recent origin, spirit and oil soluble
      4. Pontianak, semi-fossil hard, spirit and oil soluble
      5. Boea, fossil hard, oil soluble
   B. Congo, African fossil hard, oil soluble
      1. White, ivory, straw, pale, and amber
   C. Kauri, New Zealand fossil hard, oil soluble
      1. Pale and brown
      2. Bush
4. Miscellaneous resins
   A. Accroides, red gum, or grass gum, of recent origin, spirit soluble
   B. Elemi, soft of recent origin, balsam type, spirit soluble
   C. Mastic, of recent origin, spirit soluble
   D. Sandarac, of recent origin, spirit soluble

The resins are exported from the countries of origin and imported into the United States in various kinds of containers such as boxes or cases, bags or basket bags. Trade practice has standardized the packages. The botanical source, the country of origin, the packages, and the general applications are given in Table II. In the commercial grades, the term "bold" refers to the size of pieces, that is, they are large and clean. The nubs are smaller, being of the order of 2 to 4 cm. in the largest dimension. Chips and dust are primarily size classifications but decreasing size usually carries with it increasing amounts of impurities. These may be bark, twigs, or sand mechanically admixed with the resin when it formed on the trees or when it fossilized on the

ground. The term "scraped" has reference to a cleaning operation which removes surface coatings, crusty materials, or oxidized resins, while the term "unscraped" indicates that this step in grading has not taken place. The sorting and classification of the different resins are individually discussed under the chapter headings.

International standards have been developed by cooperation between exporters and importers so that gradings are done at the point of origin and trading is carried on on the basis of name designation, grade indications, and chemical and physical specifications for the products. These resins are tonnage articles of commerce whose standardization has been carried forward a very long way but which, of course, like all levels of achievement is still susceptible to considerable improvement. Standardization of names, gradings, and sizes has been carried out in the United States to a far greater extent than anywhere else in the world.

The applications of the natural resins as given in Table II are merely indicative, in that the table is not to be considered exhaustive or all-inclusive but shows the general fields. The adhesive uses are not those of water adhesives but of solvent-containing cements. The term "driers" refers to the use of siccatives in paint, varnish, and similar compositions. Varnishes as such are included under finishing compositions, and although elemi, mastic, and sandarac find some applications here, these uses are thought of as separate varnishes of a specific nature. In a similar sense, oil varnishes are set aside.

TABLE II. ORIGIN AND

Resin	Class	Tree	Country of Origin	Imported from	Package	Net Weight of Package, Pounds
Accroides		*Xanthorrhoea*	Australia, Tasmania	Australia	Bags	140
Batavia damar	Damar	*Hopea*, *Shorea*	Sumatra, Borneo, Java, East Indies	Batavia, Java	Cases	136
Batu	Damar	*Shorea*, *Hopea*, and *Vatica*	Malaya, East Indies	Singapore and East Indian ports	Bags	160
Black east india	Damar	*Burseraceae*	Malaya, East Indies	East Indian ports (Singapore)	Bags	160
Boea	Copal-fossil	*Agathis alba*	Netherlands East Indies	Macassar, Netherlands East Indies	Basket bags	160
Congo	Copal-fossil	*Copaifera*	Belgian Congo, Africa	Antwerp, Belgium	Bags	112 and 120
East india Macassar	Damar	*Dipterocarpaceae*, largely from *Shorea*	Celebes, East Indies	Macassar, Netherlands East Indies	Basket bags	175–200
East india Singapore	Damar	*Balanocarpus*, largely from *Vatica*	Sumatra, Borneo, Malaya, E. Indies	Singapore, Malaya	Cases Bags	224 160
Elemi		*Canarium luzonicum*	Philippine Islands	Manila, P. I.	Cases	80
Kauri	Copal-fossil	*Agathis australis*	New Zealand	New Zealand	Cases Bags	224–252 195
Loba (manila)	Copal	*Agathis alba*	Netherlands East Indies, Philippine Is.	East Indian ports, Manila, P. I.	Basket bags Bags	160
Manila	Copal	*Agathis alba*	Netherlands East Indies, Philippine Is.	East Indian ports, Manila, P. I.	Basket bags Bags	160
Mastic		*Pistacia lentiscus*	Island of Chios, Greece	Chios, Greece	Cases	110–140
Pontianak	Copal	*Agathis borneënsis*	Borneo	Pontianak, Borneo, Singapore	Cases (bold) Bags	Cases, 224 Bags, 160
Sandarac		*Tetraclinis articulata*	Mogador, North Africa	Morocco, Africa	Casks Bags	300
Singapore damar	Damar	*Hopea*, *Shorea*	East Indies	Singapore	Cases Bags (dust)	Cases, 224 Bags, 160–175

Applications of Natural Resins

Applications

Adhesives and cements	Amber substitute	Driers	Dry colors and pastes	Finishing compositions	Incense	Inks	Lacquers	Linoleum	Medicine	Oilcloth	Oil varnishes	Paints	Paper sizing	Plastics	Polishes	Rubber compositions	Spirit varnishes	Textile sizing	Wax compositions
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CHAPTER II

EARLY HISTORY OF THE NATURAL RESINS

Frankincense, a natural resin, was probably among the many gifts of the Magi to the infant Christ. It is certain, however, that the use of resins dates back to even greater antiquity. Examination of sarcophagi and mummified remains from a number of civilizations reveals the application of resins to this use. Mummy cases were varnished with what appears to have been a natural balsam, probably applied by the fingers when warm.

At the beginning of the nineteenth century, John[1] presented the results of his examination of specimens taken from the Temple of Jupiter Ammon (2500 B.C.?) which suggest that an oleoresin or solution of resin in oil was used. Authorities are not agreed that the oil was linseed, as no evidence exists that the Egyptians were acquainted with linseed oil, although flax was one of their crops.

Laurie,[2] through an examination of a sarcophagus of the nineteenth dynasty (1400-1300 B.C.), obtained a red resinous substance soluble in alcohol. However, as the art of distilling alcohol has been traced back only to the eighth century Arabs, one must conclude that an oleoresin or a balsam was originally used.

Tschirch and Reutter,[3] after examining resins obtained from mummies of the 1000-year period before Christ, concluded that storax, mastic, and Aleppo resin had been used. Carthaginian mummies of the same period yielded evidence of the probable use of sandarac. North African trees of this region are still the source of this resin. Examination of Phoenician mummies reveals the apparent use of amber.

Reutter,[4] in an examination of embalming resins used by the South American Incas, found evidence of the application of native balsams.

According to Pliny the Elder (A.D. 23-79), the painter Apelles (350

[1] Lieut.-Gen. von Minutoli conducted an exploring expedition in Egypt and published an account under the title "Reise zum Tempel des Jupiter Ammon, etc., nach Ober-Aegyptien in den Jahren 1820-1821." In an appendix to this book, Dr. J. F. John presented a short paper describing the historical specimens obtained.

[2] A. P. Laurie, "Materials of the Painter's Craft," G. T. Foulis & Co., Ltd., London, 1910.

[3] A. Tschirch and L. Reutter, *Arch. Pharm.*, **250,** 170 (1912).

[4] L. Reutter, *Compt. rend.,* **162,** 689 (1916).

B.C.) protected his paintings by applying a product of his own composition. As Pliny further states that the composition also imparted a lustrous appearance to the paintings, it is probable that resins were among the constituents. The Greek sculptor, Praxiteles (350 B.C.), is reported by Laurie[5] to have polished the products of his art by rubbing in resins. Soft resins such as mastic, sandarac, and olibanum were used. Pliny mentions mastic and the use of oil as a solvent for resin. Galen (second century A.D.) also mentions mastic in his writings. Theophrastus (300 B.C) discussed the electrical properties of amber. It is also referred to in various connections by Homer, Dioscorides, Vergil, Tacitus, and Pliny.

The monk Theophilus (eleventh century) is generally credited with having first written out the principles of varnish making as they are known today. In his "Schedula Diversarium Artium," Theophilus described the then current methods of varnish manufacture. The resin, probably amber, was melted to a clear liquid and added to hot linseed oil. Heating was continued until one-third of the mixture had been driven off. More hot oil was then added to bring the proportion of oil to resin to 2 to 1. Heating was continued until a drop of varnish, withdrawn and cooled, remained clear and was of the proper consistency. (Compare this with today's procedures.) Thinners were not yet used. The varnish was applied by the fingers after being warmed to obtain a workable consistency. Two centuries later, Alcherius (1338) described a similar varnish procedure.

During the Renaissance, painters adopted oil media. Rembrandt is said to have used an amber varnish as a vehicle in a number of his paints. Leonardo da Vinci is said by Vasari (1550) to have used a similar vehicle. Although resin-coated pigments are popularly considered to be one of today's innovations, four centuries ago this Florentine master was experimenting with them.

In the sixteenth century, mention is made of the use of rosin and sandarac run in linseed oil as a varnish for armor, crossbows, and harquebuses. The varnish was not thinned, being applied by sponge, finger, or stick after warming. The first account of the use of thinners in varnishes is to be found in Alberti's collection of formulae (1750). Thereafter the use of thinners soon became general. Varnish making established itself as an industry. Varnish factories were started, according to Morrell, in England in 1790, in France and Germany between 1820 and 1830, and in Austria in 1843.

[5] A. P. Laurie, "Materials of the Painter's Craft," G. T. Foulis & Co., Ltd., London, 1910.

In 1773 Watin's "The Art of the Painter, Gilder, and Varnisher" appeared and ran through fourteen editions, the last dated 1906. Following Watin's classic the literature on resins and varnishes became more numerous in proportion to the increasing technological importance of the subject, and culminated in the texts of Livache and McIntosh,[6] Sabin,[7] Coffignier,[8] Morrell,[9] and Barry,[10] among others.

Nomenclature. The English word *varnish*—or rather, its etymological forebears—originally referred to the solid resin itself. It was not until after the seventeenth century that writers were well in accord in reserving the term for the composition which today is regarded as a varnish. The English term "varnish" is taken from the French *vernis* which in turn is of Latin ancestry.

Several explanations have been advanced for the origin of the word *vernis*. One, as given by Coffignier, is that it is the combination of two Latin words: *vitrum* (glass) and *vernus ros* (spring dew). Another and more interesting explanation of the origin is that based upon the following legend.

Berenice, Queen of Cyrene and wife of an Egyptian king (Ptolemy III) who was campaigning in a foreign land, is said to have offered her beautiful golden hair as a sacrifice to insure the safety of her royal mate. According to Conon, an astronomer of that period, the hair when placed upon the altar of Venus was transformed forthwith into stars which formed the constellation known today as Berenice's Hair. The Greeks gave amber, which is also of a golden yellow color, the name "berenice." From this point on, the etymological evolution through the Latin *verenice*, the French *vernis*, and finally to the English *varnish* is readily deducible. The claim of this legend to the origin of the word "varnish" is further strengthened if the German word for amber, *bernstein*, is translated as "Stone of Berenice." The French term *vernis* becomes *berniz* in Spanish and *barniz* in modern technical Spanish. This last is quite similar to the English *varnish*. Even in Latin, the

[6] Ach. Livache and J. G. McIntosh, "The Manufacture of Varnishes and Kindred Industries," Scott, Greenwood & Son, London, Vol. I, 1904; Vol. II, 1908; Vol. III, 1911.

[7] A. H. Sabin, "Technology of Paint and Varnish," Chapman and Hall, London (1927).

[8] Ch. Coffignier, "Varnishes, Their Chemistry and Manufacture," Scott, Greenwood & Son, London (1923).

[9] R. S. Morrell, "Varnishes and Their Components," Henry Frowde, London (1923).

[10] T. Hedley Barry, "Natural Varnish Resins," Ernest Benn, Limited, London (1932).

word *verenice* is found as *veronice, vernix,* and *vernis* (Medieval Latin).

In the manuscripts of the Middle Ages, *verenice* or *veronice* was the common name for amber. Dictionaries of this period give *vernix* as being equivalent to sandarac. Amber was also referred to as "glassa" which was apparently the original German name. Recipes of Theophilus (tenth to eleventh century) and Alcherius (fourteenth century) describe the resin used as "the gum which is called Fornis," "the gum fornis which is called Roman Glassa," and as "aromatic glassa."

Toward the end of the Middle Ages writers exercised more discrimination in their designation of resins (the number of which was ever increasing) and criticized their fellow-authors for what they considered to be carelessness in terminology.

Jacobus de Thaleta (1440), in describing the preparation of varnishes, writes of dissolving two parts of gum juniper (probably sandarac) in one part of oil. In the Marciana manuscript[11] (1520) mention is made of mastic, sandarac, amber, naval pitch, and Greek pitch (rosin). Matthioli (1544) states that "the Juniper produces a resin similar to mastic called, though improperly, sandarac." Salmasius maintained that the term *vernisi* was wrongly applied to sandarac and should be reserved for amber. However, it appears that in most of the medieval works this error was very general.

Up to the time of the sixteenth and seventeenth centuries, the term *vernice* or one of its many alternative forms was applied only to the resin. It is significant that in all early accountings pigments and "varnish" were given in pounds whereas oils and other liquids were stated in gallons. Italian writers of the fourteenth century referred to the resin as *vernix* and to the fluid compound obtained by boiling with oil as *vernice liquida.* At the end of the seventeenth century the varnish resins in use were so numerous that it became better practice to refer to each one by a specific name. The words *verenice, vernix,* et al., to refer to resins fell into disuse, although *vernice liquida* continued as the term for varnish. As the consequent needless distinction between *verenice* and *vernice liquida* became apparent, writers dropped the *liquida* and adopted simply *vernice* to designate the combination of oil and resin. The eventual evolution to *varnish* has already been discussed.

In 1575 mention is made of the use of amber. The word "copal" appears to have been first used by Fra Fortunato de Ravigo (1659-

[11] "Secreti Diversi," edited by Mrs. Merrifield, 1849.

1711) in his "Secrets." Alberti (1750) describes the preparation of an amber varnish.

In 1763 B. Keane and C. Friederich were granted a patent for a varnish, the composition of which included mastic, sandarac, and elemi.

The first mention of kauri is to be found in Captain Cook's diary for November 16, 1769, although it did not become commercially important until almost eighty years later. In 1863 Frederick Walton developed his linoleum formula in which kauri was an important constituent.

Watin (1773), in his treatise mentions both amber and copals—copals reserved for the paler varnishes and amber for gold varnishes or those over dark colors. Tingry (1803) mentions copals, soft copals, and amber.

CHAPTER III

ACCROIDES

Gum accroides is the resinous product obtained from various members of the species *Xanthorrhoea* of the natural order *Juncaceae* which occurs throughout Australia and Tasmania in red and yellow forms. The resin is also known as red gum, gum acaroid, grass tree gum, "Black Boy" gum, yacca or yacka gum, and Botany Bay resin. The last-named resin is relatively scarce. The yellow variety is the product of *Xanthorrhoea hastilis*. All other *Xanthorrhoea* trees yield the red resin. The bulk of commercial red gum is obtained from South Australia and Kangaroo Island and is the product of *Xanthorrhoea tateana*.[1]

The *Xanthorrhoea* trees grow slowly and usually attain a height of 7 or 8 feet before branching into a tuft of rushlike leaves about 3 ft. in length. The trunks are composed of a fibrous, pithy material surrounded by a jacket approximately 3 in. thick formed by the dying off of old rushlike leaves. The charring of this leafy jacket during forest fires leads to the name of "Black Boy."

The resin accumulates at the base of the dead leaves along the stem and is collected by stripping the enveloping husk from the core with an axe. Occasionally the husk may be sufficiently soft to permit easy removal, but more frequently it is a hard coherent mass which must be mechanically separated from the core. The proportion of resinous husk to the core, which varies with the season, is less in winter than in summer.[2] The cut should not be made directly to the core of the tree, as the leaf bases are then cemented together in large blocks which are subsequently rejected in the sieving operation. On the other hand, when a series of shallow cuts are made, the leafy bases are sufficiently reduced in size to make separation from the resin difficult. The cutting requires considerable skill and should be to such a depth that the leaf bases separate readily. Chopping off the crown of the tree is the cus-

[1] A. R. Penfold, "Grass Tree Resin," Technological Museum of Sydney, *Bull. No. 16* (July, 1930).

M. F. N. Halloway [*J. Proc. Sydney Tech. Coll. Chem. Soc.*, **7**, **41-53** **(1935-37)** (Pub. 1938)] has described the chemical and physical properties of resins obtained from various species of *Xanthorrhoea*.

[2] J. L. Strevens, "The Technology of Grass Trees," *Chem. Eng. Mining Rev.* (January to June, 1921).

tomary, though unnecessary, practice. When the crown of the tree is uncut, removal of the husk seems to have little effect upon the tree, provided that sufficient resin is left to protect the core. Even when "lopped," the tree frequently recovers. The husks fall into frameworks placed about the base of the tree. They are then collected and subjected to a sieving operation in a "jigger," which removes most of the leaf bases and any large lumps of caked husk, as well as separates the resin into two grades. The jigger consists of an inclined sieve of wire netting (½- to ¾-in. mesh) above an inclined metal sheet containing smaller perforations. A horizontal shaking motion is imparted to the gratings while the husks are fed in through a hopper at the top. A winnowing operation separates any leaf bases remaining with the coarse gum.[3]

The collection of accroides is subject to licensing according to the district in which the resin is to be collected. The quantity of resin obtainable from an individual tree appears to vary with the species from which collected, and possibly with other factors. Estimates of different collectors vary from 2 to 4 lb. or lower to upwards of 40 or 60 lb.[4, 5, 6] A similar situation is met with the amount of resin collected per man per day. Estimates range from 25 to 100 lb.

The sieving and winnowing method of purifying accroides is subject to high losses of resin. Methods designed to avoid these losses have been studied. A procedure in which the mixed gum and leaf bases are placed on sieves in a steam-heated vat has been in commercial operation. The molten resin runs into trays and is later removed to cooling receptacles. Residue from the screens is utilized as fuel. The product contains but little foreign matter and the yield of resin is increased by one-third over the jigger process, but the tree dies as the result of the lopping and stripping operations employed. The slow growth of the tree, however, makes it desirable that collection methods should not result in its destruction. Solvent extraction methods[7] have also been employed for the purification of accroides. Patents[8] have been granted for a method of purification in which the resin is dissolved in a dilute alkaline solution, filtered, and then precipitated with acid. By proper control of the temperature during precipitation, the resin is obtained in a granular condition which can be easily handled.

[3] J. C. Earl, "Grass Trees," *Bull. No. 6,* Dept. of Chemistry, South Australia, Commonwealth of Australia, 1917.

[4] H. G. Smith, *Tech. Gazette New South Wales,* **9,** Part I (1919).

[5] J. C. Earl, *Loc. cit.*

[6] J. L. Strevens, "The Technology of Grass Trees," *Chem. Eng. Mining Rev.* (January to June, 1921).

[7] H. J. Pooley and J. L. Strevens, British Patent 150,638 (1919).

[8] H. C. Miller and H. A. Irlam, British Patent 103,006 (1916).

Approximately seventeen varieties of the tree are known, but commercial distinction is made only between the yellow and the more prevalent red gum. The gradings of accroides are according to color, particle size, and material which is produced as a result of screening, with the commercial grades yellow, red gum coarse, and red gum powdered. The red gum is usually in the form of small dusty pieces of a reddish brown color which is exported in bags of 140 lb.

Accroides differs from the other natural varnish resins in that it contains appreciable quantities of free benzoic and cinnamic acids and is thus closely related to the balsams. The resin is of the alcohol-soluble type and is insoluble in aryl and aliphatic hydrocarbons. Like the manilas, both varieties are soluble in alkali. The alcohol solution of red accroides gradually deposits benzoic acid upon standing. The yellow variety also contains benzoic acid obtainable by acidifying the alcohol solution with hydrochloric acid.

The composition of yellow and red accroides has been studied by a number of investigators. The results obtained are listed in the table of resin constituents on page 20. Both varieties contain a resin-tannol which yields picric acid upon nitration. The yield which varies according to the species of *Xanthorrhoea* from which the resin is obtained, is of the order of 50 per cent for the yellow and from 5 to 50 per cent for the red variety.[9] A number of processes have been suggested, and the preparation of picric acid and nitrophenols from accroides has been patented.[10] Small yields and high nitric acid consumption do not permit economic competition with chemical production of picric acid from phenol or chlorobenzene. The belief has been expressed, however, that appreciable quantities of accroides were utilized for the preparation of explosives by Germany during the First World War.

The constituents of accroides are also suitable as the starting point in the synthesis of certain organic dyestuffs. Treatment with sulfuric acid or with sulfur in the presence of an alkali has been patented[11] as a means of producing brown and black dyes.

Attempts to bleach accroides in a manner similar to shellac have been unsuccessful. Simion[12] reported the bleaching of red accroides in acid solution but found that the color returned upon standing. His alcoholic solution of the yellow resin gradually darkened to the color

[9] H. G. Smith, *Tech. Gazette New South Wales*, **9**, Part I (1919).

According to *Bull. Imp. Inst.*, **18**, 154-62 (1920), the yields of picric acid are 30 per cent from the yellow resin and 25 per cent from the red.

[10] H. C. Miller and H. A. Irlam, British Patent 104,352 (1917).

[11] H. C. Miller and H. A. Irlam, British Patent 104,353 (1917).

[12] F. Simion, *Chem. Ztg.*, **47**, 141 (1923).

TABLE III

CHEMICAL COMPOSITION OF ACCROIDES

Constituent	Formula	Basicity	Per Cent	Remarks
p-Coumaric acid	$HOC_6H_4CH:CHCOOH$ (*p*-oxycinnamic acid)			These results are for red accroides, the characteristic resinotannol of which is erythro-resinotannol, $C_{40}H_{39}O_9OH$
Free (1)		Mono	1	
Combined with benzoic and cinnamic acids and a tannol (1)			2	
p-Oxybenzaldehyde (1)			0.6	
Resinotannol (1)			85	
p-Coumaric acid	$HOC_6H_4CH:CHCOOH$ (*p*-oxycinnamic acid)			These results are for yellow accroides, the characteristic resinotannol of which is xanthoresinotannol, $C_{43}H_{45}O_9OH$
Free (1)			4	
Combined with tannol (1)			7	
Cinnamic acid	$C_6H_5CH:CHCOOH$			
Free (1)			0.5	
Combined with tannol (1)			0.6	
Styracin and probably the phenyl propyl ester of cinnamic acid (1)			1	
p-Oxybenzaldehyde and probably vanillin (1)			0.6	
Resinotannol (2)			80	
p-Coumaric acid	$HOC_6H_4CH:CHCOOH$ *p*-oxycinnamic acid)			
Free (2)		Mono	0.5	
Combined (2)			1.5	
Cinnamic acid (2)	$C_6H_5CH:CHCOOH$	Mono	0.1	
Styracin (2)			0.1	

(1) A. Tschirch and K. Hildebrand, *Arch. Pharm.*, **234,** 698 (1896).
(2) *Bull. Imp. Inst.*, **18,** 155 (1920).
See also: Nagai, *Ber.* **24,** 2847 (1891); E. H. Rennie, W. T. Cook, and H. H. Finlayson, *Trans. Chem. Soc.*, **117,** 338 (1920); H. H. Finlayson, *J. Chem. Soc.*, 2763 (1926).

of the red gum solution when exposed to air. Gardner and Parkes[13] applied the usual hypochlorite method for bleaching shellac to accroides but did not obtain satisfactory results.

Penfold[14] studied the removal of coloring matter and insolubles from accroides by solvent extraction methods. He found that use of benzol as the solvent in a modified Scott extraction plant yielded a superior resin containing much less coloring matter and tannins than the crude resin. The product was stated to be directly applicable to the resin industry without need for further bleaching or refining. The purified resin may be bleached directly with chlorine, or in solution by the use of peroxides. The bleached resin is stated to be suitable for the manufacture of sealing wax and pale ester gums. It was also reported that the process involved very low costs for fuel, power, and labor and that solvent losses were less than 1 per cent of the charge treated.

Accroides differs markedly from the other natural resins in that it is the only material which, as marketed, is heat-reactive in a manner analogous to that of the heat-reactive phenol-formaldehyde resins. When heated to thermal processing temperatures, the resin is converted into hard, completely insoluble, and unusually resistant films. Manila and Congo copals possess similar properties under specific conditions, but not in the form in which they are marketed. Owing to its heat-reactive properties, accroides is not adapted to the preparation of oil varnishes. Accroides is compatible with cellulose acetate and cellulose nitrate, but not with ethyl cellulose.

The low price and heat-reactive properties of accroides have a definite influence upon its commercial use. One application is as a binder in the preparation of wallboard. It is a substitute for rosin in paper coating and for shellac in spirit varnishes, lacquers, and printing inks. The resin is also used in the preparation of finishes for cellulosic materials, metals, metal foil, and glass as well as in the preparation of molding powders from phenol-formaldehyde resins.[15] Livache and McIntosh[16] mention concentrated solutions of red accroides plasticized with castor oil or balsam as a red coating for windows of photographic laboratories to exclude the active rays of the sun.

[13] H. A. Gardner and H. C. Parkes, *Paint Mfrs. Assoc. Circ. 201* (March, 1924).

[14] A. R. Penfold, "Grass Tree Resin," Technological Museum of Sydney, *Bull. No. 16* (July, 1930).

[15] German Patent 462,838 (1936).

[16] Ach. Livache and J. G. McIntosh, "Manufacture of Varnishes and Kindred Industries," Vol. 3, p. 237, Scott, Greenwood & Son, London (1911).

CHAPTER IV

CONGO

Congo resins are among the hardest of natural resins. In their original form, congos, unlike other copals, are considered to be insoluble in practically all organic solvents, although with a number of these, gelatinous liquids or transparent viscous gels may be formed. The untreated resin is likewise insoluble in varnish oils.

The analytical constants may be summarized in the following average figures:

Direct acid number	100
Saponification number	125
Iodine number	125
Melting point (mercury method)	140–200°C. (depending upon grade)
Specific gravity	1.05
Refractive index	1.540

For the constants of individual grades, reference should be made to Chapter XII.

When thermally processed or "run," congo becomes soluble in petroleum solvents of all varieties, coal-tar solvents, alcohols such as butanol, esters such as butyl acetate, ethers, certain ketones, as well as fatty acids and varnish oils. After running, the resin is compatible with ethyl cellulose, nitrocellulose, a wide variety of other resins of a natural and synthetic nature, waxes, pitches, and asphalt. The original unrun resin can be incorporated with a considerable number of waxes at temperatures of the order of 275 to 325°C. It is largely compatible with stearic acid at temperatures in the range of 150 to 200°C.

Run congo with nitrocellulose gives lacquers which are very hard, which sand readily and show high wear resistance. The resin and nitrocellulose are compatible over a wide range of resin-nitrocellulose ratios. Run congo is also compatible with ethyl cellulose and chlorinated rubber.

Tests have shown that run-congo finishes are free from odor. The taste and odor of so sensitive a substance as butter was unimpaired by one week's direct contact with the resin film. This commends the use

of run congo in paper finishes and printing inks for food containers where this property is a specific.

Congo resins are adaptable to a wide range of varnish products. This is their chief field of application. Congo is the "universal" resin of the varnish maker. Varnishes prepared with it are equal or superior to those containing well-known modified-phenolic resins in the matter of durability, elasticity, weather resistance, color retention, and drying time. An outstanding property of congo varnishes is the manner in which the film weathers. Tests have demonstrated that congo varnishes (in common with most natural resins) weather in a manner (very fine checks) that requires little or no labor to prepare a surface for revarnishing. On weathering, modified-phenolic varnish films suffer wide cracking and present surfaces which demand laborious preparation for revarnishing. Moderation and elimination of this shortcoming of modified-phenolic resins can be affected by Congo resin additions.

The gloss and "depth of film" of congo varnishes are highly prized. For this reason, congo has long been the standard rubbing-varnish resin. Manufacturers of synthetic resins fortify their products in these properties by the incorporation of Congo resin.

Thermally processed congo imparts excellent adherence to varnishes and finishing compositions when these are applied to metal surfaces. Its use is called for in a number of governmental specifications for decorative and protective coatings applied to metal surfaces subjected to severe atmospheric service.

Congo was the first resin to be used in the preparation of so-called "wrinkle finishes."

Because of its high acid number, congo cannot be used for vehicles for paints or enamels containing reactive pigments. Insoluble "soaps" are formed because of a neutralization reaction. This is known as "livering" and the danger of its occurring exists whenever the acidity of a resin is great enough to cause a reaction with basic pigments. Depending upon the reactivity of resin and pigment, livering may result in the formation of a "cheesey" mass or merely in an increase in consistency.

When congo is esterified with glycerin or other polyhydric alcohols, congo esters or copal esters are formed. Congo esters have low acid values and are free from "livering" tendencies. In addition to good heat, moisture, dilute acid and alkali resistance, they possess several advantages. These include color retention at high baking temperatures, bleaching of the varnish film upon aging, non-toxicity, absence

of the impartation of taste or odor to aqueous liquids and solutions with which they may come in contact, complete solubility in cheap petroleum solvents, stability during varnish making, and the ability to improve the drying of linseed oil.

These processed copals can be dissolved in varnish oils by heating with the oils to approximately 500°F. They are also soluble in a wide variety of solvents.

Congo esters have been on the American and European markets for a number of years. In addition to their use in oil varnishes, they are finding wider application as furniture, food container, toy, tray, and other lacquers which must withstand heat, moisture, and the action of dilute acids and alkalies.

The properties, uses, and manufacture of congo esters are discussed fully in the chapter on chemical modification of natural resins (Chapter XVI).

Like tung oil, and more recently, oiticica oil, congo did not immediately win the favor which it subsequently acquired. Compared with the easy-melting kauri then in vogue, congo was a difficult resin to run and the first attempts to utilize it in varnish making did not yield satisfactory results. The poor initial results obtained were understandable, for the varnish makers tried to run congo in the same manner in which they processed kauri. The result was a resin showing incomplete or unstable solubility in oils. When it was once realized that congo required higher processing temperatures (650°F. as compared to 600°F. for kauri) as well as a slightly longer heating period, the resin was adopted by varnish manufacturers.

Running of Congo resin and properties of the product are discussed in the chapter on thermal processing (Chapter XV).

Classification. The African copals used in the United States are now sold under the designation of congo and are obtained from the Belgian Congo. The exploitation of the copal deposits along systematic lines has reduced the price and increased the output to such an extent that the copals of this area possess almost a complete monopoly on the African copal trade. In recent years upwards of 97 per cent of the African copal exports originated in the Belgian Congo.

Such names as Zanzibar, Accra, Benguela, Angola have just about disappeared from the American market and the American varnish maker's vocabulary. In 1934 the American importers and the Belgian exporters agreed to classify the copal taken from the Belgian Congo as follows:

COMMERCIAL GRADES OF CONGO RESINS

White and ivory

1 Water-white transparent
2 Cloudy white
14 Selected fully scraped ivory
15 Ordinary ivory sorts
16 Inferior ivory sorts
24 No. 1 Ivory nubs
25 No. 2 Natural ivory nubs

Straw colored

3 Selected pale straw bold
4 Pale bold straw
5 Pale bold straw
7 Pale straw bold washed
18 Pale straw nubs
19 Pale straw nubs

Amber

6 Pale amber bold
8 Light amber bold
9 Medium light amber bold
10 Rescraped hard dark amber
11 Hard dark amber bold
20 Dark hard amber nubs

Sorts and selections

12 Selected sorts bold
13 Dark sorts bold
21 Selected nubs ordinary
22 Small mixed nubs
23 Dark mixed nubs

Pale

17 No. 1 Pale fingers
26 Bold pale chips
27 Small pale chips
28 Pale dust

The congos have been grouped as to color into grades known as white and ivory, straw, pale, and amber, as well as mixed designations of sorts and selections. Within each grading, individual resins also carry numbers as hardness designations; the lower the number the harder the resin. In several instances, individual resins also have names indicating surface conditions such as "fully scraped," "rescraped," and "washed" (an alkaline wash). The terms bold, nubs, chips, and dust are size classifications. Sorts are grades containing a number of colors. Fingers indicate a shape which is similar to that of the human finger.

The resins as gathered and packed in containers by the native (without regard to color, size, or cleanliness) are known as "tout venant." It is this mixture that is usually purchased by large processors of congo for the manufacture of copal esters and run congo.

According to origin, Congo resins may be divided into three classes: (1) recent resin obtained directly from the living tree through either accidental or deliberate wounding; (2) semi-fossil resin found in the soil, having dropped from still existent trees; (3) fossil resin deposited in the ground by trees which may or may not have ceased to exist. The contributions of the first two sources are small.

Collection. In the Belgian Congo, the chief source is the tree *Copai-*

fera demeusi Harms. Other trees closely related to this also produce copal but to a much smaller extent.

The resin is actively collected from the numerous tributary valleys along the east bank of the Congo River between Stanleyville and Leopoldville. This area, once the bed of an inland sea, is alternately a sandy and a marshy region most of which is flooded during part of the year. Collection of resin begins immediately after the waters have receded and before the ground hardens, with the chief collecting period beginning in April and ending in July. The ground is still ankle-deep in mud when the natives set up camp in the area to be worked. The men hunt and fish to provide the camp with food but do not engage to any great extent in the actual resin collecting. This is done by the women and children. Armed with long metal-tipped lances, the natives traverse the region, prodding the ground until they strike a piece of resin. The resin is then extracted and carried in baskets on the backs of the natives to the camp where the resin is dried in the sun and freed by hand of earthy impurities. The deposits are usually found at depths of a few inches to three feet. Deposits deeper than this exist but are not worked by the natives because of the greater labor involved, as well as their difficulty of location.

A good collector can obtain from 50 to 80 pounds of resin a day. The average, however, is about half of this. Approximately 80 per cent of the copal exported from the Belgian Congo is dug from the ground in this manner. Accumulations are also found in the river beds, where they have been washed from the soil by the periodic rise and fall of the water level. This source has never been worked exhaustively. Another minor supply is obtained from the accidental wounding of still existent congo-producing trees but systematic tapping apparently is not practiced. All Congo resin imported into the United States is of the fossil type taken from the earth and the river beds.

After the preliminary cleaning done at their camp, the natives pack the congo to a collecting station where it undergoes a second rough cleaning operation. The final cleaning and grading operations are done at the commercial distributing centers.

Steeping the resin in dilute caustic soda solution of about 1 per cent strength to remove surface dirt was formerly common practice. More recently, a process for cleaning congo by sandblast has been developed by van der Tailen and the Société Coloniale Anversoise.[1] In this method the resin is placed in a rotating drum fitted with a perforated bottom through which the finer dust falls. A sandblast, passed through

[1] British Patent 309,254 (1928).

the slowly rotating drum, rapidly removes the adherent impurities. Baffles are placed within the drum to insure a more even distribution of the sanding action. The congo dust so formed can be removed from the sand by water-floating.

A modification substitutes iron filings for the sand. The iron is then removed from the copal dust by a magnetic separator.

In addition to the mechanical advantages of speed and ease of handling, this method produces a resin that has undergone no chemical contacts and is therefore of a very high degree of purity. A wide range of Congo resins can be produced, the palest of which are almost colorless.

The congo dust obtained is considerably soluble in alcohol-ketone combinations. Cold-cut solutions containing 35 per cent of actual resin have been prepared and are satisfactory for quick-drying traffic paints.

During the First World War, importers of Congo resins undertook the direct importation of "tout venant" from the Belgian Congo and in a short time had set up machinery for the grinding of the resin. The gradings were matched to the types formerly shipped from Antwerp. After the war, Antwerp resumed its normal position and the emergency American activity was discontinued.

Constitution of Congo Type Resins. The chemical composition of a number of copals of the congo type has been studied by various investigators. Acids and resenes have been isolated and their formulae have usually been determined and names assigned.

This work has been summarized in Table IV. Unfortunately, such investigations are subject to serious limitations and it would be difficult to prove that all the "acids" and "resenes" claimed by their discoverers are definite, individual compounds.

In several instances the work of independent investigators gives results that tally. For example, Bauer and Gonser (1926) have isolated from Congo resin an acid identical in melting point and formula with the congocopalic acid of Tschirch and Engel (1908). The original discoverers considered it to be monobasic ($C_{19}H_{30}O_2$), although the later investigators claimed it to be dibasic ($C_{38}H_{60}O_4$). In the light of later work on the thermal processing of Congo resins by Hellinckx,[2] it would appear that the latter is correct. It is probable that many of the acids in Table IV, designated by their discoverers as monobasic, are actually dibasic.

[2] L. Hellinckx, "Studies on Congo Copal" (1935); "Pyrogenation of Congo Copal" (1938), Bruxelles, Librairie Falk fils Georges van Campenhout, Successeur, 22, Rue de Paroisiens, 22.

TABLE IV

Composition of Congo Type Resins

Constituent	Formula	Basicity	Melting Point °C.	Per Cent	Remarks
Zanzibar copal					
Trachylolic acid (1)	$C_{54}H_{85}OH(COOH)_2$	Di	165–168	80	Lead salt insoluble in alcohol.
Isotrachylolic acid (1)	$C_{54}H_{85}OH(COOH)_2$	Di	105–107	4	Lead salt soluble in alcohol.
α-Resene (1)	$C_{41}H_{68}O_4$			6 (α- and β-Resene together)	Soluble in ether. Optically active.
β-Resene (1)	$C_{25}H_{38}O_4$				Insoluble in ether. Optically inactive.
Volatile essential oils (1)				3	
Congo copal					
Congocopalic acid (2)	$C_{19}H_{30}O_2$	Mono	115–118	48–50	
Congocopalolic acid (2)	$C_{21}H_{33}OCOOH$	Mono	108–110		
α-Congocopalresene (2)				12 (α- and β-Congocopalresene together)	
β-Congocopalresene (2)					
Essential oil (2)				3–4	
An acid (3)	$C_{38}H_{60}O_4$	Di	115–118		This acid is identical to the congocopalic acid above, but was considered by the investigators to be dicarboxylic.
Benguela copal					
Bengucopalic acid (2)	$C_{19}H_{30}O_2$	Mono		43–45	Same formula as given for congocopalic acid.
Bengucopalolic acid (2)	$C_{21}H_{32}O_3$		114–116	22	A homologue of congocopalolic acid.
α-Bengucopalresene (2)				4–5	
β-Bengucopalresene (2)				14–16	
Cameroon copal					
Cameroucopalolic acid (4)	$C_{21}H_{36}O_3$	Mono	98–100		
α-Cameroucopaloresene (4)					
β-Cameroucopaloresene (4)	$C_{25}H_{38}O_4$		225		
Essential oil (4)			Boiling Point 145–155		d. 0.830.
Angola copal					(Results are from analysis of red angola.)
Angocopalolic acid (4)	$C_{23}H_{36}O_3$	Mono	85		Unsaturated. Lead salt only slightly soluble in alcohol.
An acid impossible to purify (4)					Lead salt soluble in alcohol.
α-Angocopaloresene (4)	$C_{30}H_{54}O_6$		63–65		
β-Angocopaloresene (4)	$C_{25}H_{38}O_4$		220–224		
Essential oil (4)			Boiling Point 140–160		
Sierra Leone copal				20	
Leonecopalic acid (5)	$C_{25}H_{48}O_3$	Mono	142	30	Iodine No. 64.8–65.2. Lead salt insoluble in alcohol.
Leonecopalolic acid (5)	$C_{21}H_{38}O_2$	Mono or poly	133	15	Iodine No. 76.7–79.6. Lead salt insoluble in alcohol.
Leonecopalinic acid (5)	$C_{14}H_{24}O_2$		184	8	Iodine No. 110–111.7. Lead salt soluble in alcohol.
α-Leonecopaloresene (5)	$C_{14}H_{26}O_2$			20	
β-Leonecopaloresene (5)	$C_{14}H_{26}O_2$		195	1–2	
Volatile oil (5)				5	
A vegetable mucilage (5)				2–3	Insoluble in water.
Ash (5)					

TABLE IV (*Continued*)

Constituent	Formula	Basicity	Melting Point °C.	Per Cent	Remarks
Loango copal					
α-Loangocopalic acid (5)	$C_{20}H_{36}O_2$	Mono	134	18	Iodine No. 78.4–80.4. Lead salt insoluble in water.
β-Loangocopalic acid (5)	$C_{15}H_{30}O_2$	Mono	56	12	Lead salt insoluble in alcohol.
Loangocopalolic acid (5)	$C_{18}H_{34}O_2$	Mono	60	25	Iodine No. 87.7–88.1. Lead salt insoluble in alcohol.
Loangocopalinic acid (5)	$C_{24}H_{44}O_2$	Mono	165	15	Iodine No. 70.2–71.6
α-Loangocopaloresene (5)	$C_{23}H_{46}O_2$			5	
β-Loangocopaloresene (5)	$C_{23}H_{46}O_2$		200		
Essential oil (5)			Boiling Point 160	5	
Ash (5)				3	
Benin copal					
Benincopalic acid (6)	$C_{17}H_{22}O_4$	Mono	137		Iodine No. 83.5. Lead salt insoluble in alcohol.
α-Benincopalolic acid (6)	$C_{13}H_{32}O_6$	Mono	81		Iodine No. 87.2. Lead salt insoluble in alcohol.
β-Benincopalolic acid (6)	$C_{20}H_{30}O_2$	Mono	119		Iodine No. 84.2. Lead salt insoluble in alcohol.
Benincopalenic acid (6)	$C_{27}H_{48}O_2$	Mono	101		Iodine No. 63.9.
α-Benincopalinic acid (6)	$C_{21}H_{30}O_3$	Mono	187		Iodine No. 76.5.
β-Benincopalinic acid (6)	$C_{15}H_{28}O_3$	Mono	193–197		Iodine No. 97.8.
β-Benincopalresene (6)	$C_{12}H_{30}O_{10}$		192–195		
γ-Benincopalresene (6)	$C_{13}H_{26}O_4$				
Accra copal					
Accracopalic acid (6)	$C_{21}H_{34}O_3$	Mono	104–106		Iodine No. 75.3.
α-Accracopalolic acid (6)	$C_{18}H_{32}O_2$	Mono	152–155		Iodine No. 85.5.
β-Accracopalolic acid (6)	$C_{19}H_{32}O_2$	Mono	144–158		Iodine No. 86.9.
α-Accracopalenic acid (6)	$C_{10}H_{20}O_2$		142–146		
β-Accracopalenic acid (6)	$C_{12}H_{20}O_3$		150–152		
Accracopalinic acid (6)	$C_{14}H_{26}O_3$	Mono	122–144		Iodine No. 98.3.
α-Accracopalresene (6)	$C_{15}H_{36}O_6$		178–180		
β-Accracopalresene (6)	$C_{13}H_{26}O_3$		197–199		
γ-Accracopalresene (6)	$C_{10}H_{20}O_3$		184–186		
Brazil copal (South American)					
Brazilcopalic acid (7)	$C_{24}H_{40}O_3$	Mono	170–175	6	
Brazilcopalolic acid (7)	$C_{22}H_{38}O_2$	Mono	95–100	24	
Brazilcopalinic acid (7)	$C_{16}H_{30}O_2$	Mono		17	
α-Brazilcopaloresene (7)				4	
β-Brazilcopaloresene (7)				8	
Essential oil (7)			Boiling Point 245–255	5	
Ash (7)				8	Rather high percentage, indicating a dirty sample.
Colombia copal (South American)					
Colombiacopalic acid (7)	$C_{22}H_{40}O_3$	Mono			
Colombiacopalolic acid (7)	$C_{22}H_{40}O_2$	Mono			
α-Colombiacopalinic acid (7)	$C_{14}H_{24}O_2$	Mono			
β-Colombiacopalinic acid (7)	$C_9H_{20}O_3$	Mono			
Volatile liquid (7)			Boiling Point 210–220 (in vacuo)	12	Odor similar to turpentine.

(1) A. Tschirch and Stephan, *Arch. Pharm.*, **234,** 552 (1896).
(2) A. Tschirch and A. Engel, *Arch. Pharm.*, **246,** 293 (1908).
(3) K. H. Bauer and K. Gonser, *Chim. Umschau,* **33,** 250 (1926).
(4) M. Rackwitz, *Bull. soc. chim.*, **II,** 135 (1909).
(5) M. Willner, *J. pharm. chim.*, **II,** 128–9 (1910); *Oil Colour Trades J.*, **1910, p. 2225.**
(6) A. Tschirch and M. Kahan, *Arch. Pharm.*, **248,** 433 (1910).
(7) M. Machenbraum, *J. pharm. chim.*, **I,** 362–3 (1912).

Tschirch and Engel after examining Congo and Benguela copals have pointed out an apparent relationship between the two. Both congocopalic and bengucopalic acids have the same formula, ($C_{19}H_{30}O_2$), while bengucopalolic ($C_{21}H_{32}O_3$), congocopalolic ($C_{22}H_{34}O_3$) and angocopalolic acids ($C_{23}H_{36}O_3$) are homologues. It is interesting to note the similarity in the formulae of congocopalic acid ($C_{19}H_{30}O_2$) and abietic acid ($C_{20}H_{30}O_2$).

In explanation of the presence of unfamiliar, or no longer current, resins in Table IV, it should be remembered that resins of these names were common at the time the investigations were conducted. The resins listed are quite similar in botanical origin and general properties to the Congo resins of today, but for various reasons have been almost completely supplanted by the latter.

In addition to its esterification by combination with polyhydric alcohols and fatty acid glycerides, congo is capable of being acetylated to yield a product known as "acetocopal," which is suitable for varnish manufacture and as a lacquer plasticizer. By similar treatment with butyric acid, "butyrocopal" can be obtained which possesses kindred properties and uses. These chemical modifications are discussed in detail in Chapter XVI.

CHAPTER V

DAMAR

The damars constitute a class of considerable commercial importance. Damar imports to the United States are from 15 to 20 million lb. annually.

The resins vary in color from a strong yellow to almost water-white, generally clear or only slightly opalescent. Damar films show no yellowing but on the contrary bleach to colorless films upon exposure to sunlight. Damar is characterized by having the lowest acid number of any important natural resin, this value rarely exceeding 37 or 38 and in commercial samples generally running from about 25 in the best grades to about 35 in the poorest. The resin is, therefore, non-reactive and is well suited for applications utilizing pigments of an alkaline nature.[1]

The damars are of the hydrocarbon solubility type, being soluble in petroleum and coal-tar solvents, hydrogenated naphthas, terpenes, and chlorinated solvents. They are only partially soluble in alcohols. Together with the related east indias, the damars constitute a class of natural resins which are directly soluble in drying oils by simple heating without thermal processing. The damars also show a wide range of compatibility with other resins, waxes, cellulose derivatives except the acetate, pitches, oils, and similar materials. The extended range of solubility and compatibility contributes much to their usefulness in industrial fields.

In cellulosic lacquers the light-colored damars impart the necessary adhesive qualities in addition to improving the gloss and hardness and preventing the occurrence of after yellowing. For this purpose the damar must undergo a "dewaxing" operation. Likewise the damars are modifying agents for alkyd resins, whether in clear or pigmented coatings, and have proven to be equal to the maleic-anhydride-rosin resins used for that purpose. The inclusion of damar in alkyd baking enamels markedly improves color retention and often gloss and hardness. In addition, damar has the advantage of suitability for use with reactive pigments for which the maleics are not satisfactory. In other respects

[1] C. L. Mantell and H. L. Rubenkoenig, "The Origin, Application, and Properties of Damar," *Paint, Oil Chem. Rev.*, June 11, 1936, p. 28.

it is almost impossible to distinguish between the resulting enamels. It is not necessary that the damar be dewaxed for this purpose. Damar also finds similar uses in the cheaper rosin and rosin ester enamels.

Damar possesses the property of fume-proofness to a high degree and is used as an ingredient of fume-proof enamels. The non-reactive nature, light color, and bleaching properties of damar have made it an indispensable ingredient for the formulation of such materials as luminous paints, overprint varnishes, and transparent oil varnishes in which the tendency of other resins to yellow upon aging is highly objectionable. The damar films may be hardened, if desired, by incorporating small amounts of a phenolic resin in the varnish at some sacrifice of freedom from after yellowing.

The pale color, high gloss, and ready solubility in low-priced hydrocarbon solvents have resulted in a large number of applications for damar spirit varnishes, providing articles such as toys and cheap jewelry with a bright and attractive finish for quick sale and short life, for spraying citrus fruit to improve gloss and reduce shrinkage from evaporation, for transparent window envelopes, for coating hard candies, and for preparing shellac substitutes.

In the field of plastics, damar has been found to impart very desirable molding characteristics as well as light color and has been utilized in the preparation of injection molded objects, molding powders, and rubber compositions. Damar has also been used in a similar sense as plasticizer for the linoxyn used in the manufacture of linoleum and oilcloth. Furthermore, damar may be combined with synthetics to produce a resinous material directly soluble in drying oils without thermal processing.

When emulsified with water, damar is used in the preparation of no-rub floor and furniture polishes, printing inks, medications such as salves and ointments, in color photography, and, when pigmented, as a dressing for white shoes and other leather accessories. In combination with other materials such as waxes and chlorinated rubber, damar is a constituent of chemically resistant coatings, waterproofing compositions, impregnating media for paper, cardboard and textile fabrics; matches and pyrotechnic materials; waxes for dance floors; and adhesives for various purposes.

The damars are recent resinous exudations of trees of the *Dipterocarpaceae* family (the fruit of which have wings) and more specifically of the species *Hopea* and *Shorea*. The damar-producing trees are indigenous to the Malay Peninsula and the western islands of the East Indian archipelago. However, the damars of commerce, in so far as the

United States is concerned, come almost exclusively from the islands of Sumatra and Borneo in the Netherlands East Indies. The word "damar" in the Malay States and the East Indies originally referred to a torch made by mixing leaves and bark with powdered resin.

Damars are designated by their point of entrance into commerce rather than by their geographical source. There are three principal ports of export: Batavia on the northwest coast of the island of Java, Singapore on the Malay Peninsula, and Padang on the west coast of Sumatra. The damars of southern Sumatra, together with a portion of the damar produced in Borneo, are sent to Batavia for export while damars from the northern and eastern portions of Sumatra, together with the remainder of the damar from Borneo, are graded and exported at Singapore. Damar from the west coast of Sumatra enters commerce at the port of Padang and hence is known as Padang damar.

Two varieties of damar are graded at Batavia depending upon whether the resin originated in Sumatra or Borneo. The varieties are designated as Sumatra damar and Pontianak damar, respectively, and for export purposes are designated as Batavia damar.

The collection of damar and its preparation for market is not the result of haphazard and unorganized native trading. Like the collection of other Netherlands Indies natural resins, it is a well-organized industry operating under the rigid supervision and with the full cooperation of the Netherlands Government. Collection, grading, sorting, preparation for market, and distribution of the product are systematically conducted and are strictly comparable to the methods of industries utilizing natural raw materials such as rubber, naval stores, sugar, palm oil, coconut oil.

According to the Laboratorium voor Scheikundig Onderzoek at Buitenzorg, Java, some fifty-five species of damar-producing trees have been catalogued. In certain regions, as many as ten species may contribute to the damar produced in that locality. The predominance, however, is from one or two species which are present in sufficiently high proportions to insure the contributions from other species a negligible importance. The supervision of collecting and sorting enforced by the Colonial Government of the Netherlands East Indies has resulted in such uniformity in the exported resin that two damar samples of the same grade seldom show variations of more than one or two points in such characteristics as acid number, iodine number, melting point.

In thickly populated districts and near the villages the damar-producing trees have been cut down to clear the land for agricultural purposes. In easily accessible wooded areas, the trees have been killed

by indiscriminate tapping and other abuses prior to government supervision. It is therefore usually a journey of a day or more for the native to reach the interior of the tropical forests and the particular section of trees that he is working.

Courtesy C. van de Koppel

Fig. 8. Notch and dome method of tapping and collecting damar resin from *Shorea javanica.*

The resin is secreted by the sapwood upon either accidental injury or the systematic tapping which is necessary for constant production. Regular production and satisfactory yields of resin are not usually attained until after two or three tappings. The diameter of the tree

determines the number of tap holes. The tapping usually consists of from two to four vertical series of ten or more tap holes approximately 20 inches above each other, often reaching a height of 50 feet or half the height of the bole of the tree. The hole itself is a semicircular incision in which the exuded resin collects. In tapping and collecting, the

Courtesy C. van de Koppel

FIG. 9. Tree heavily tapped for damar.

native, with the aid of a loop of rattan tied around his body and encircling the trunk of the tree, and with the tappings as footholds, climbs the tree much as a lineman ascends a telegraph pole.

Collection of the resin usually occurs at intervals of from three to six months, although in some instances collections may be made as early as one month after tapping. A normally producing damar tree in southern Sumatra yields from 4 to 6 lb. of resin two or three times a year or a total of from 8 to 18 lb. per year. The large trees of Borneo have a much higher rate of production and sometimes yield as much as 40 to 50

lb. of resin per year. After each collection a portion of the wood is cut away from the tapping to make a fresh opening of the resin ducts. The collected resin is then usually dried in the shade for a period of a week or more prior to delivery to the village merchant.

The method by which the collection of damar is financed is of interest. The village merchant obtains an advance payment from the resin merchant, who is usually located at the point from which the resin is exported. The village merchant in turn makes an advance payment to the owner of the trees who may or, more usually, may not work his own trees. The villagers employed by the owner to collect the resin are frequently not paid in money but receive a portion of the resin (varying between one-third and two-thirds) in payment for their services. In Borneo the trade in damar often follows the rivers up which the traders travel by small boats carrying merchandise to be bartered for damar and other products.

After delivery of the unassorted damar at Batavia or Singapore, the resin is scraped, screened, sorted, graded, and packed for shipment. The following grades of damar are commercially available.

Batavia Damars	*Singapore Damars*
Batavia damar A/E standard	Singapore damar No. 1
Batavia damar A/D mixed	Singapore damar No. 2
Batavia damar A	Singapore damar No. 3
Batavia damar B	Singapore damar chips
Batavia damar C	Singapore damar seeds
Batavia damar D	Singapore damar dust
Batavia damar E	
Batavia damar F	
Batavia damar dust	

The gradings of Singapore damar are on the basis of color and freedom from impurities, the No. 1 being the lightest or most nearly white. This grade is translucent but almost transparent. Numbers 2 and 3 are less transparent and have some color. The designations chips, seeds, and dust are primarily size classifications, but decreasing size usually carries with it increasing amounts of impurities.

The letter designations of Batavia damar are primarily size classifications and secondarily those of color and impurities, the amount of which usually increases with decreasing size. The grades refer to the material retained on the specified screens as given below. The A material is that retained on an A screen; B material, that which goes through the A screen and is retained on the B; C material is that which passes through the B screen and is held back by the C screen; D material, in a

similar manner, that which passes through the C screen and is retained on the D; and E material, often known as seeds, that which passes through the D screen and is retained on the E sieve, while an F mate-

Courtesy C. van de Koppel

FIG. 10. Sorting Batavia damar.

rial and dust are products passing through the E screen. The F grade is dirtier than E and is composed of splinters rather than seeds.[2]

The A grade contains about 0.1 per cent non-resinous matter, the

[2] Specifications for the wire screens used in grading Batavia damar are as follows:

A Steel, woven-wire poultry netting, ½-in. hexagonal mesh, 21 gage wire, galvanized after weaving.

B 3 square holes per linear inch, steel wire #17 Washburn & Moen gage, diameter 0.054 in., screen opening 0.279 in.

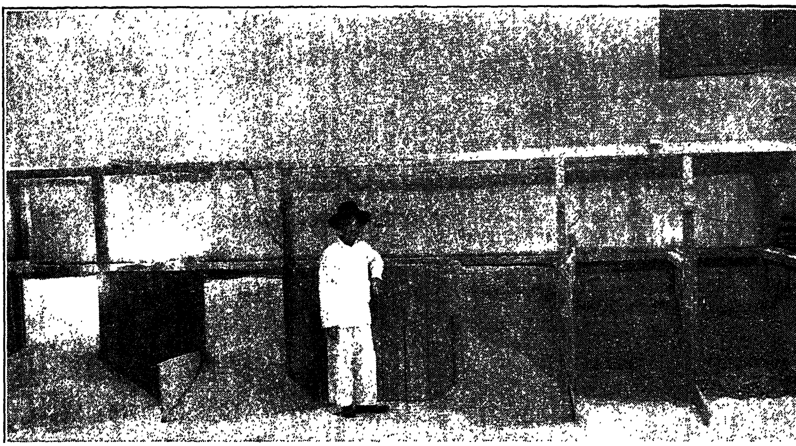
C 6 square holes per linear inch, steel wire #19 Washburn & Moen gage, diameter 0.041 in., screen opening 0.126 in.

D 10 square holes per linear inch, steel wire #20 Washburn & Moen gage, diameter 0.035 in., screen opening 0.065 in.

E 40-mesh, brass wire cloth #30 Birmingham gage, diameter 0.012 in., screen opening 0.013 in.

B, C, and D grades but slightly more, whereas the F grade may contain 3.5 per cent and the dust 4 to 6 per cent.

In the Malay States and Netherlands East Indies varieties of damar are designated by names which are usually taken from the district in which the particular resin originated. In addition to this, the semi-fossil resins of the damar type, known in this country as the east indias, are also designated as damars in the Far East. The results are somewhat confusing as it is often difficult to trace these resins from their source into the final Batavia and Singapore classifications. Inasmuch



Courtesy C. van de Koppel

FIG. 11. Storage bins for damar showing, from right to left, A, B, C, D, and E grades.

as the native classifications are not encountered in the United States, it is felt that their discussion in this text would lead to unnecessary confusion. The more important native designations are listed in the appendix. Adequate descriptive treatment can be found in the earlier literature.

Damar is exported from Batavia in cases of 136 pounds net weight and from Singapore in cases of 224 pounds. Dust shipped from Singapore is in bags weighing from 160 to 175 pounds. Since the resins are of recent origin, they are relatively soft in the resin scale of hardness. In the commercial grades they show softening points of the order of 155 to 170°F. and melting points by the mercury method of 210 to 235°F.

Commercial grades of damar have been compared with one another in their solubility in various solvents. The solubility, as indicated by the viscosity of the solutions, varied but little from one grade to the

other. The viscosity of the lowest grade seldom exceeded that of the highest grade by more than 0.5 poise in a 1 to 1 solution.

Experiments have also shown that aside from greater color and cloudiness in the lower grades, clear varnishes and lacquers from the various grades show practically no differences. Hardness, flexibility,

Courtesy C. van de Koppel

Fig. 12. Batavia damar prepared for export.

gloss, drying time, and tackiness of the film are practically the same for all grades. Grinding zinc oxide into spirit solutions of the resins gives enamels which are indistinguishable from one another.

The chemical composition of the damars has been studied by a number of investigators. The more important results obtained will be found in Table V.

In general, damar resin consists of two resin acids and an α- and β-resene together with small amounts of an essential oil which is apparently of a terpenic nature. The resin acids can be obtained by extraction with hot dilute sodium hydroxide solutions followed by precipitation with mineral acid. The two resenes may be separated by

TABLE V

CHEMICAL COMPOSITION OF DAMAR

Constituent	Formula	M.P. °C.	Per Cent	Remarks
Dammarolic acid (1)	$C_{56}H_{80}O_8$ or $C_{54}H_{77}O_3 \cdot OH \cdot (COOH)_2$		23.0	
α-Resene (1)	$C_{11}H_{17}O$ or $C_{24}H_{34}O_2$	65	40.0	Batavia damar
β-Resene (1)	$C_{31}H_{52}O$	206	22.5	
Water (1)			2.5	
Ash (1)			3.5	
Impurities (1)			8.0	
Losses (1)			0.5	
Dammarylic acid (2)	$C_{36}H_{60}O_3$			
Dammaryle (a terpene) (2)	$C_{10}H_{16}$			
Dagincoleic acid (3)	$C_{22}H_{44}O_4$	170	35	A Borneo damar called "damar duging" by the natives
Dagingenoleic acid (3)	$C_{13}H_{26}O_3$	125–126	15	
Resene (3)	$C_{22}H_{28}O$		16	
Oil (3)		B.P. 165–200	15	
3 Acids	$C_{16}H_{26}O_2$ (4)	135	18	A Borneo damar apparently of semi-fossil nature
	$C_{14}H_{32}O_2$ (4)	103–105	25	
	$C_{12}H_{18}O_2$ (4)	120–122	18	
Volatile oil (4)			8	
An acid	$C_{11}H_{20}O$ (4)		3	
A resene	$C_{12}H_{22}O_2$ (4)		15	

(1) A. Tschirch and Glimmann, *Arch. Pharm*, 1896, p. 585.
(2) These results are attributed to Franchimont but no reference is given.
(3) E. Gottlieb, *Bull. soc. chim.*, **II**, 719 (1912).
(4) E. Gottlieb, *Bull. soc. chim.*, **II**, 720 (1912).
Also see: A. Zinke and E. Unterkreuter, *Univ. Graz Monatsh.*, **39**, 865–9 (1918); *J. Chem. Soc.*, [I], **116**, 166.

extraction with ethyl alcohol, in which the α-resene dissolves leaving the β-resene as a residue.

The β-resene, which is usually termed "damar wax" in the lacquer trade, is the only constituent of the resin which is not at least largely soluble in the common lacquer solvents. It is therefore necessary to treat the resin by a "dewaxing process" in order to remove the β-resene

prior to use in the formulation of lacquers. The dewaxing process usually consists of dissolving the resin in a suitable solvent and precipitating the β-resene or wax by adding methyl or ethyl alcohol. Various extraction methods have been proposed, but the precipitation method remains the only one in wide use.

Both the nature of the solvent used and the grade of damar affect the character of the precipitate obtained. For the better grades of damar the best results are obtained by following the widely used procedure of dissolving the resin in an equal weight of toluol and adding an equal weight of alcohol. For the poorer grades, however, the toluol is better replaced by a mixture of two-thirds light petroleum naphtha and one-third ethyl acetate, or by ethyl acetate 12.5 per cent, acetone 12.5 per cent and benzene 75 per cent.

By increasing the proportion of damar to as much as two and one-half parts, the toluol procedure may be made to give good results with all grades of damar. The wax-free solution is of low viscosity, about 0.5 poise (A on the Gardner-Holdt scale) and because of its low solvent content—about 45 per cent—is adaptable to a wider variety of lacquer formulations.

The actual β-resene content of damar resin varies from 8 per cent to 11 per cent. Generally in dewaxing damar there is a total loss of 15 to 20 per cent, as some of the solution is occluded in the precipitate. In general, Singapore damar may contain more wax than the Batavia grades and give slightly redder solutions. The dewaxed damar is soluble, or largely soluble, in nearly all the common organic solvents.

The β-resene or damar wax obtained as the by-product of the dewaxing operation possesses a number of interesting properties. The purified β-resene possesses the inertness characteristic of resenes in general. It has a very low acid number (2 to 4) and cannot be saponified, hydrolyzed, or esterified. As might be expected, removal of the low acid value resene imparts a higher acid value to the damar. This increase is not marked in the β-resene but becomes appreciable if the more prevalent α-resene is also removed.

The purified β-resene has a high melting point, ranging from about 200 to 210°C. according to the grade of resin and method of dewaxing. It is soluble in a wide range of hydrocarbon solvents. The wax dissolves readily in linseed oil when heated to above its melting point but precipitates out on cooling. However, with additional cooking a clear solution is obtained which does not cloud on cooling. Cooking the oil and wax together for half an hour at 290 to 300°C. will give a clear product, the brilliance of which may be increased by further cooking.

The incorporation of the damar wax increases the viscosity tremendously. The product from 35 per cent purified damar wax and 65 per cent of raw linseed oil has a consistency only slightly less than that of gum elemi. Additional cooking at 290 to 300°C. does not perceptibly change the body of the product but does impart a more brilliant clarity. Lowering the percentage of damar wax to 25 or 20 per cent and cooking it into raw linseed oil produces varnishes of suitable consistencies for printing ink formulation. The β-resene prolongs the gelation time of tung oil slightly and again greatly increases the viscosity.

In cold-cut varnishes and enamel vehicles, damar wax markedly increases the viscosity as well as serves as a flatting agent. The action of damar wax as a flatting agent is peculiar in that it is extremely effective even in small amounts and yet when present as a constituent of damar itself does not result in a loss of gloss.

The relationship of dewaxed damar and damar wax in spirit varnishes (using solvents such as toluol) is shown by the fact that increasing β-resene content will result in increased viscosity and film hardness together with decreased flexibility and adhesion.

Purified β-resene has also the interesting property of high resistance to wetting with water. This property is so marked that if a layer of powdered damar wax be dusted over the surface of a beaker of water, it is then possible to immerse a finger in the liquid and subsequently remove it entirely dry. This property naturally suggests the use of damar wax as the repellent for various types of waterproof coatings.

Damar wax as a by-product of lacquer manufacture is available in large quantities. Unfortunately, however, the wax is in an unpurified condition and, as such, is largely used as a cheap filler in various industrial processes. The possibilities of the material have therefore not been fully realized by many technicians.

In addition to the damar components obtained by dewaxing processes, other modifications of raw damar are possible. Although low in acid value and non-reactive as a varnish constituent, damars and damar acids can be esterified with small amounts of glycerine to produce materials similar in properties to the ester gums but darker in color. These products are characterized by even greater solubility than the original resins. Damar can also be acetylated to produce a product of exceptional resistance to alkali.

The damar-producing trees on occasion yield an opaque resin known as "dead damar," damar mati, and a number of other designations. The resin produces cloudy solutions and may be troublesome to the varnish maker. The cause of the opaqueness is not known and apparently

varies in different samples. It has been attributed both to high moisture content and to high acid value but neither claim has been substantiated, inasmuch as dead damar samples having subnormal moisture contents and acid values have been reported. It has been established, however, that water contents in excess of about 2 per cent will cause formation of cloudy solutions. Dead damar tends to be even less soluble than normal damars in alkaline solutions.

The cause of dead damar formation is uncertain, although it is most frequent in first tappings and with immature trees. The product is easily recognized and rarely is found to any extent in commercial damar. When dewaxed, damar mati yields clear solutions as suitable for use in lacquer formulations as those from normal resin.

CHAPTER VI

THE EAST INDIAS: BATU, BLACK, AND PALE

The East India resins are divided into three classes: pale east india,[1] black east india, and batu. All are derived from trees of the same family which produce the Batavia and Singapore damars. Unlike the latter,

Courtesy C. van de Koppel

FIG. 13. Sorting and grading East India resins.

however, the East India resins are of greater age and hardness. They are not tapped but are collected by the natives from places where they fall or are transported. East India resins may be considered to be semi-fossilized damars and are classified as hard damars.

Although all three classes possess kindred properties, each sells at a different price level because of differences in color, ease of handling, and solubility.

The east indias are low acid value resins, all being in an average range of 20 to 30. Their softening and melting points, similar and con-

[1] Pale east india is marketed in two grades, hiroe, exported from Macassar, and rasak, exported from Singapore.

siderably above those for ordinary damar, are from 110 to 125°C. and 140 to 160°C., respectively. Of the three groups, batu has the highest melting point.

Collection. The East India resins, although damars, are not tapped from the trees, but are collected by the natives where found as a result of accidental wounding or normal exudation.

In Borneo several names have been given to the batu resins found there according to the place of origin. Batu means stone, and the expression "damar batu" indicates that the resin is found as stones or pebbles are found and not that the pieces physically resemble stones. Other significant native names are: damar batu "genung" (*genung*, mountain), damar batu "laut" (*laut*, sea), damar batu "pasir" (*pasir*, sand), and damar batu "aer" (*aer*, water).

Damar batu genung is found in dry places, i.e., in or on the soil, but the other three are collected from places to which they have been transported by water. These may be found at the seashore (damar batu laut), in sand banks of rivers or former river beds (damar batu pasir), or perhaps in the water—river or sea (damar batu aer).

In former river beds quite sizeable deposits are found. Usually the pieces of resin have attained a rounded form similar to river pebbles, but under the influence of long water immersion, the surface is in a more or less deteriorated condition. From such varieties of batu, much resin must be scraped off to obtain a marketable quality. The genung variety, on the other hand, lacking the water exposure of the other batus, is much harder and requires but a minimum of surface cleaning.

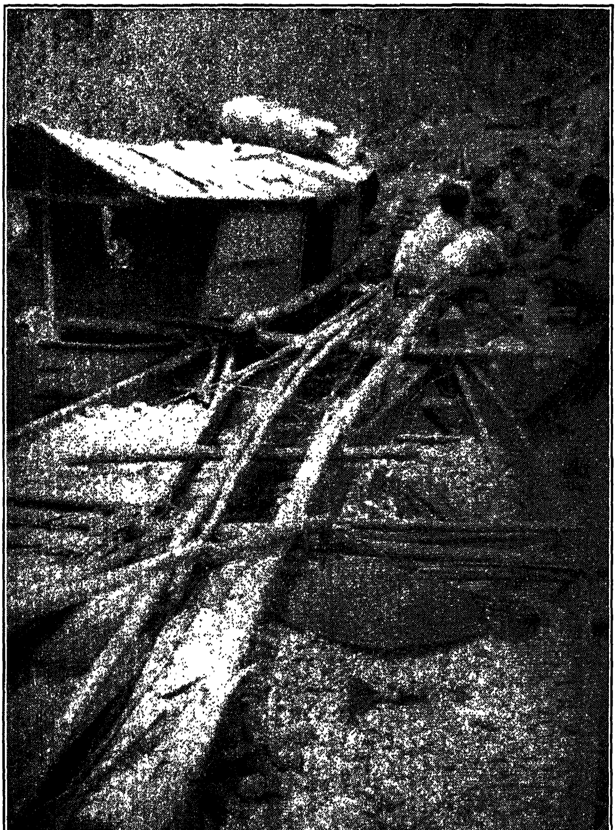
It is impossible to state the age of batu resins for it is not known how long ago these resins fell to the ground and were transported by water and deposited. Batu resins frequently contain a considerable amount of water which must be removed. This is usually done by the importer.

Some rasak and hiroe resins also are collected in the same localities as batu, but these are found for the most part on the tree or at its base. Both rasak and hiroe have the advantage of being quite uniform, originating from one or two tree species only. Batu is always a mixture of resins from quite a number of different tree species, including those of *Shorea*, *Hopea*, and *Vatica*.

The black East India resins are found on trees as well as in the earth or water (being transported in the manner of the batus). Black East India resins can easily be distinguished from other varieties of east india by their black color as well as their peculiar grayish dust coating. Although the resin approaches the color of coal, clear varnish films of a

satisfactorily light color are obtained. The resin is also known as damar "hitam," hitam being the Malayan word for "black."

Uses. If one overlooks differences in color, viscosity, and cost, along with slight changes in handling, almost any one of the East



Courtesy C. van de Koppel

FIG. 14. Transportation of East India resins in boats.

India resins can be used in the same formula. It would therefore be repetitious to discuss their applications separately. The East India resins are used in floor varnishes, grinding vehicles, priming coats for metal, enamels, sanding sealers, mill whites, and as vehicles for oil-base traffic paints. In floor varnishes and traffic paints, East India resins are particularly suitable as they show outstanding resistance to abrasion and chipping. These properties are discussed in the varnish

chapter. Excellent but inexpensive spar varnishes can be formulated with East India resins.

East India vehicles show the best leafing properties of all the natural resins when used in aluminum paints.

These resins have been found to improve markedly the adhesion of rubber cements to wood, leather, and cloth, and are added in the form of petroleum naphtha solutions.

Linoleum cements showing good bonding properties are prepared by mixing a low-grade, batu-petroleum naphtha solution with an inert filler of fuller's earth or a similar cheap mineral or pigment.

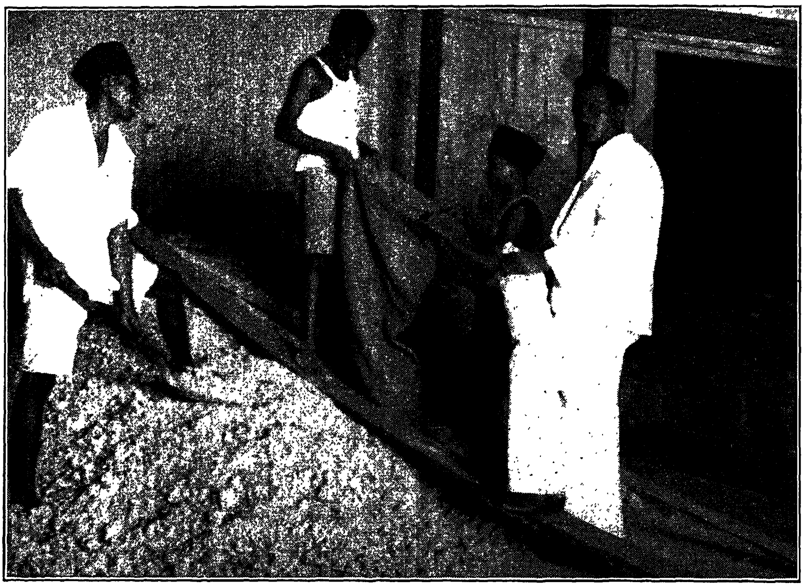
An interesting application of batu involves plasticizing the resin with linseed oil to bring the melting point down to the neighborhood of boiling water. Bodied linseed oil heated with batu over a 10-minute period to 500°F. with a loss of 5 per cent, produced a combination of 25 per cent batu and 75 per cent linseed oil, which was a very sticky, viscous semi-liquid that would not harden rapidly nor dry for several weeks' time. The material found employment as marking media on textiles, and later could be removed readily during a washing operation. Combinations of the order of 50 to 60 per cent batu and 40 to 50 per cent linseed oil with negligible loss of weight of the resin were very soft and very tacky, and melted in boiling water. These products are useful as semi-permanent adhesives.

In a search for a cheap, alkali-resistant ink varnish, a combination of batu and tung oil has given some very favorable results. The batu was run, then cooked with tung oil just enough to dissolve safely, then thinned with heavy petroleum thinner to the proper body. One batch of resin was run in an open kettle, another in a closed kettle, with both heat treatments a little more severe than customary. The proportions of oil to resin used were 3 to 2 plus about 0.75 to 1.0 part of thinner and 1 to 1 plus about 1 to 1.25 parts of thinner. The resin run in the closed kettle was found to impart slightly better alkali resistance.

BATU

Batu is a semi-fossil or semi-recent East India resin related to the damars but differing in several important characteristics. It is readily soluble in coal-tar hydrocarbons and in hydrogenated aliphatic or petroleum solvents, as well as in a number of high-solvency petroleum fractions. The viscosity of its solutions is commonly much greater than that of damar. This property is valuable for the manufacture of cements, gasketing materials, and related products.

Batu may be readily dissolved in an inexpensive solvent consisting of a minimum of 15 per cent benzol and a maximum of 85 per cent petroleum thinner. The benzol is added to the resin first and then half of the petroleum thinner is added. The resin is dissolved preferably in a mixing machine and when homogeneity is reached, the other half portion of the petroleum thinner may be added. Decreased viscosity of



Courtesy C. van de Koppel

FIG. 15. Bagging batu.

the solutions may be obtained by the use of hydrogenated petroleum fractions.

Batu shows compatibility with stearic acid and with a wide range of waxes, oils, resins, asphalts, and pitches. It is an inexpensive resin whose softening point in commercial grades is from 250 to 270°F. and melting point by the mercury method 320 to 360°F. Its acid number by the direct method varies from 20 to 40. Batu shows slight incompatibility with cellulosic derivatives with most solvent balances.

Like the damars, it may be incorporated in oils by simple heating without previous thermal processing. It is useful for flat varnishes of both the oil and spirit type.

The principal sources of batu are the Celebes and Borneo. The resin appears in the following commercial grades:

Batu scraped
Batu unscraped
Batu nubs and chips
Batu chips
Batu dust

Batu resins are opaque and usually quite light in color, predominantly yellow. When fresh it is usually of a dark brown color which bleaches with age to the light yellow form.

BLACK EAST INDIA

Black east india is a dark-colored resin related to the damars, semi-recent in its origin, but more closely allied with the pale East India and batu resins. Its acid number range is of the same order as the damars, its softening point range of the same order as the east indias. Its melting point, covering a range of 320 to 330°F., is higher than pale east india. Its solubility characteristics are similar to the east indias, and its applications are of the same type. It is sometimes called damar hitam, or black damar.

Black east india finds application in dark-colored varnishes, gloss paints, printing inks, plastics and oilcloth, and adhesives. Black east india varnishes when first applied are quite dark in color but rapidly bleach to transparent films comparable with varnishes made from very light resins. Black east india oil varnishes show good alkali resistance. The resin is compatible with stearic acid and a host of waxes, oils, resins, asphalts, and pitches, but if not dewaxed, it is an unsatisfactory lacquer resin.

The principal sources of black East India resins are Java and Madoera, and to a smaller extent, Malaya. The resin is marketed in grades of:

Black bold scraped
Black bold unscraped
Black nubs and chips

Black east indias are quite black and are sometimes covered with a grayish powder. Films containing this resin, however, are of satisfactory lightness.

PALE EAST INDIA

The pale East India resins are semi-fossil or semi-recent materials related to the damars. They are designated as pale East India of

Macassar packing, sometimes referred to as hiroe, and the pale east india of Singapore packing, often termed rasak. Like the damars, they may be incorporated in oils without previous thermal processing, inasmuch as they show solubility in hot oils. They are commonly incorporated by heating directly in the vegetable oils employed in varnish making.

The Macassar type shows a softening point range from 214 to 250°F. and a melting point range of 260 to 310°F. The direct acid numbers range from 16 to 35, with a somewhat narrower range for the Singapore packing, the softening and melting points of which are of the same order as the Macassar type. The pale east indias are compatible with other resins, with oils, with asphalts, with petroleum, coal-tar, and vegetable pitches, with waxes, as well as with nitrocellulose and ethyl cellulose save that very slight incompatibility may be met with some solvent balances.

The hiroe[2] variety is exported from Macassar and is collected from the Moluccan Islands and Borneo. The rasak variety is collected from Borneo and Malaya and exported from Singapore. Rasak is produced principally from the *Vatica* species, hiroe principally from the *Shorea* species. Actually, pale east india Singapore contains a portion of hiroe whereas pale east india Macassar contains a portion of rasak.

The commercial gradings of the Macassar and Singapore varieties of pale east india are identical. These are

Pale east india bold
Pale east india nubs
Pale east india chips
Pale east india dust

The pale East India resins of Singapore packing are dark red or brown in color. The Macassar variety is usually reddish-yellow and paler than those of Singapore packing.

Generally, the resins of Singapore packing appear to be more soluble in petroleum solvents than those of Macassar packing. This is evidenced by the greater clarity of the Singapore solutions as well as by the greater amounts of resin dissolved.

The pale east indias also differ in their wax content, the Singapore variety possessing the greater amount.

[2] H. Kemner, "Hiroe Damar, Its Constants and Possible Uses in the Varnish Industry," *Farben-Ztg.*, 41, 586 (1936).

E. Stock, "Resin Studies XXXIII—Further Studies on Hiroe Damar," *Farben-Ztg.*, 43, 582-3 (1938).

Solubility. In solubility the East India resins are quite similar to the damars, the same general solvents being suitable, although the former's lesser ease of solution is indicated by greater viscosity or even incomplete solubility in certain petroleum thinners of low aromatic contents. All are completely soluble in coal-tar solvents, hydrogenated aliphatic hydrocarbons, and petroleum thinners of sufficient aromatic strength. Alcohols, esters, and ketones are not solvents for East India resins, serving merely to swell or soften the resin when used in equal weight portions. Such terpenic solvents as turpentine or dipentene dissolve pale east indias but do not dissolve batu or black east india.

Solubility determinations performed on fresh and old (i.e., a sample in warehouse storage for a number of years) samples of batu revealed the older sample to be the more soluble in petroleum solvents. Thirty-two petroleum solvents were investigated and eighteen of these proved to be solvents for old batu, while only eight were solvents for the new.

The chief apparent difference between old and new batu lies in their moisture contents. Once the moisture content has been reduced to a certain level, further aging or drying has little effect on solubility, save in the matter of viscosity. This has been verified by running solubility tests on samples of varying ages as well as on oven-dried specimens.

To offset the effect of excessive moisture present in new batu, it is necessary to use a lower-boiling solvent than would ordinarily be demanded by an older and drier sample.

The East India resins possess a portion of inert bodies (resenes) similar to damar wax, but the amount of wax obtained by a dewaxing process (e.g., solution in toluol followed by the addition of alcohol) is considerably in excess of the amount formed from damar. Dewaxing losses for damar are from 15 to 20 per cent, whereas with East India resins the following losses were obtained by the authors:

	Per Cent
Batu scraped	50
Batu nubs and chips	49
Batu dust	51
Black east india bold scraped	56
Black east india unscraped	55
Black east india nubs and chips	54
Pale east india—Macassar bold	44
Pale east india—Macassar nubs	40
Pale east india—Macassar chips	38
Pale east india—Macassar dust	36
Pale east india—Singapore bold	53
Pale east india—Singapore nubs	48
Pale east india—Singapore chips	41

The alcohol-soluble fraction forms clear solutions in most organic solvents and yields glossy films. The alcohol-insoluble fraction is insoluble in all but a few solvents and in those gives cloudy, viscous solutions, and dull films.

The wax obtained appears to be similar to that from damar, i.e., low acid value and high melting point. The dewaxing of east indias represents a source of damar wax should the demand for this exceed the amount obtained from the dewaxing of damar.

Compatibility with Nitrocellulose. With most solvent balances the slight incompatibility of the east indias does not impair the integrity or adhesion of the lacquer film. Incompatibility usually takes the form of varying degrees of cloudiness in the dried film. Advantage is taken of this property in the preparation of flat lacquers.

CHAPTER VII

ELEMI

Elemi is the resinous product obtained from the tree known as *Canarium luzonicum*, a member of the *Burseraceae* family. The tree is indigenous to the Philippine Islands and particularly to the island of Luzon. A number of other tree species of the *Burseraceae* family[1] produce elemis in various parts of the world, but the resins, other than that from the Philippines, are of little commercial importance.

Tschirch and Cremer[2] studied the resinous product obtained from the tree *Canarium commune*, a native species of India. They were unable to detect any difference between this material and the elemi of commerce, and therefore assumed that the Philippine resin was the product of this same species. The assumption is incorrect.

Elemis would be classified as oleo-resins, since they possess a higher content of essential oil than the other natural resins. The Manila elemi of commerce is a soft, sticky, opaque, greenish- or yellowish-white material with a pasty consistency which can readily be deformed by pressure with the fingers. It has a spicy, somewhat bitter taste and a fragrant terebinthinate odor. When exposed to air for extended periods of time, it gradually hardens throughout and becomes brittle. The softening and melting points of commercial elemi are below room temperature. The acid number of the resin shows a range of 30 to 35 and its saponification number is of the order of 20 to 40.

Elemi is completely soluble in coal-tar hydrocarbons and esters but not in petroleum solvents, alcohols, and ketones. Addition of about 5 per cent of a coal-tar hydrocarbon to the alcohol solution will result in complete solubility. More specifically, elemi is soluble or largely soluble in *sec*-amyl, benzyl, and *n*-butyl alcohols, chlorobenzene and chloroform, coal-tar hydrocarbons, amyl acetate, butyl acetate, butyl butyrate, butyl propionate, ethyl abietate, isopropyl acetate, ethyl ether, terpineol, the alcohol-ethers, glycol monoacetate, carbon disulfide, ethylene glycol diethyl ether, ethylene oxide, glycol diacetate, hexalin, phenol, propylene oxide, and tetralin.

[1] Merrill, "The Source of Manila Elemi," Publ. Bur. Govt. Labs., Manila, **29**, 51-5 (1905).

[2] A. Tschirch and Cremer, *J. Chem. Soc.*, 812A (1902); *Arch. pharm.*, **260**, 293 (1902).

It is partly or slightly soluble in denatured ethyl alcohol, diacetone, isopropyl and methyl alcohols, chlorinated compounds other than chlorobenzene and chloroform, butyl lactate, dimethyl phthalate, ethyl acetate, methyl salicylate, octyl acetate, ethers other than those given above, ketones, dipentene, turpentine, diethylene glycol monoacetate, Cellosolve acetate, acetic acid, glycol ether acetate, tricresyl phosphate, paraffin, and hydrogenated petroleum solvents.

Elemi differs from the other natural resins in that it consists of finely divided crystalline material dispersed throughout a resinous matrix. Partial solubility, as in alcohols, acetone, and similar solvents, frequently indicates solubility of the matrix with subsequent deposition of the insoluble crystalline material from solution. At normal temperature and in the absence of excess solvent this deposition may amount to 25 per cent of the resin. The phenomenon of crystalline deposition from alcohol solution together with high essential oil content are characteristics common to the elemis from all sources.

Elemi is compatible with vegetable, fish and animal oils of the drying and non-drying types; waxes of the mineral and vegetable variety, as well as stearic acid; and with cellulose derivatives such as nitrocellulose and ethyl cellulose, although it shows a slight incompatibility with cellulose acetate. It is readily compatible with the phenol aldehyde resins of the 100 per cent, modified, and heat-reactive type, as well as rosin, ester gum, maleic-rosin resins, and the paracoumarone materials. It is readily miscible with petroleum asphalts; petroleum, coal-tar, and vegetable pitches, as well as fatty acids. In the preparation of resin-wax combinations, it often serves as a mutual solvent or flux.

Elemi finds application as a plasticizer, conferring increased adhesion to lacquers applied to metal surfaces; in adhesives and cements, wax compositions, printing inks, surface coatings applied to textiles and paper, linoleum and oilcloth, as a base in perfumery, as an ingredient in water-proofing compositions, as well as in engraving and lithography. It has also been utilized in the preparation of salves and plasters for medicinal purposes, and as a plasticizer in the manufacture of hats, spirit varnishes, and bronzing liquids. When added in small quantities to lacquers and spirit varnishes, it markedly improved the ease of brushing as well as adhesion and flexibility.

The collection of the resin by the natives in the Philippine Islands has been described by Clover[3] as follows:

[3] "The Terpene Oils of Manila Elemi," *Philippine J. Sci.*, **11** [A], 1-40 (1907).

The tree *Canarium luzonicum* is widely distributed in the Philippines and is known to the Tagalogs as "pili." Pili resin is commonly known by the Spanish term "brea" which is applied by the natives indiscriminately to all similar products. The resin is obtained by removing a narrow strip of bark horizontally about the trunk of the tree in four or five different places. A thin transparent fluid soon appears about the exposed part and in time becomes somewhat viscous and opaque. The amount of resin increases for a month or so, gradually falling several inches below the cut and in time taking on the appearance of a cataract. If the resin is not frequently removed, it hardens on the outside and generally takes on a yellowish color. Often several accumulations of at least 10 pounds of resin occur on large trees, probably within a few months. For commercial purposes the resin is required to be as soft, clean, and colorless as possible, so with this in view, it is carefully removed from the tree at definite intervals and not allowed to accumulate. When a tree is continuously used for resin it is customary about once a year to remove the bark for a couple of inches above the last cut. Many trees are to be found which have evidently been long employed in this manner and which give evidence of this gradual removal of the bark for several feet up and down the trunk. The resin finds considerable use among the natives as an illuminant, for which purpose it is rolled in a palm leaf, or better, in the fibrous part of the trunk of the young coconut tree. For such purposes it behaves very similar to pine pitch, and a large torch of it, used especially by fishermen, gives a light which can be seen at a great distance and which burns for many hours.

Elemi is shipped in tin-plate containers (usually paper-lined for ease of handling) which contain 80 lb. of resin.

Elemi contains 20 to 25 per cent of essential oils, 13 to 19 per cent of acids, about 30 to 35 per cent of resenes, and 20 to 25 per cent of alcoholic resinols, terpenic in nature. The fresh resin contains about 5 per cent water, which decreases rapidly with the length of time the resin is exposed to air. A large amount of investigative work upon the composition and properties of the constituents of elemi has been carried out. The more important data will be found in Table VI.

Elemi has been much studied from the viewpoint of pure organic chemistry, as a number of its constituents have been found to be of use as starting points in the synthesis of complex organic substances.

The amyrins and the bryoidines have been of particular interest in the study of natural products related to phenanthrene.[4]

[4] L. F. Fieser "The Chemistry of Natural Products Related to Phenanthrene," 1937, Second Edition, Reinhold Publishing Corporation, New York.

TABLE VI

Composition of Elemi

Constituent	Formula	Basicity	Melting Point °C.	Per Cent	Remarks
α-Amyrin (1)	$C_{30}H_{50}O$		181–181.5		Westerberg concluded that these were probably secondary alcohols
β-Amyrin (1)	$C_{30}H_{50}O$		193–194		
α-Amyrin (2)	$C_{30}H_{45}OH$		183–184		
β-Amyrin (2)	$C_{30}H_{45}OH$		193–194		
Manamyrine (3)	$C_{25}H_{42}O$		177	20–25	
Maneleresene (3)				30–35	
α-Manelemic acid (3)				5–6	
β-Manelemic acid (3)				8–10	
Essential oil (3)				20–25	
Bryoidine (3)	Fluckiger $2C_{10}H_{16}3H_2O$			0.8–1	
Ash and bitter substance (3)				1–2	
Impurities (3)				5–6	
Manamyrine (3)	$C_{25}H_{42}O$		177	20–25	
Maneleresene (3)				30–35	
α-Manelemic acid (3)				5–6	
β-Manelemic acid (3)				8–10	
Essential oil (3)				7–8	
Bryoidine (3)	Fluckiger $2C_{10}H_{16}3H_2O$			0.8–1	
Ash and bitter substance (3)				1–2	
Impurities (3)				15–20	
Briene (4)	$C_{30}H_{48}(OH)_2$		216–217		
A monatomic alcohol closely related to amyrin					
Amyrins (2-cryst.) (5)	$C_{30}H_{45}O_8$			20–25	
Resenes (5)				30–35	
Acids (5)				13–19	
Essential oils (5)				20–35	
Impurities (5)				7	

(1) A. Westerberg, *Ber.*, **20,** 1242 (1887). *Ber.*, **23,** 3186 (1890). *Ber.*, **24,** 3834 (1891).
(2) A. Tschirch and Cremer, *J. Chem. Soc.*, 812A (1902).
(3) A. Tschirch and Cremer, *Arch. pharm.*, CCLX, 293 (1902).
(4) A. Westerberg, *Bull. soc. chim.*, **11,** 1456 (1907).
(5) A. Zinke, F. Frederich, and A. Rollett, *Monatsh. Chem.*, **41,** 253 (1920).
(6) O. Wallach and Reindorff, *Ann. chim.*, 1892.
(7) A. Zinke, F. Frederich, and A. Rollett, *Monatsh.*, **42,** 477 (1921).
(8) A. Rollett and H. Schmidt, *Monatsh.*, **45,** 510 (1924).
(9) M. Mladenovic, *Bull. soc. chim. roy. Yougoslav.*, **5,** 57–62 (1934).
(10) F. S. Spring, *J. Chem. Soc.*, 1933, 1345–6.
(11) H. Lieb and M. Mladenovic (with A. Rezak and M. Sabotka), *Bull. soc. chim. roy. Yougoslav.*, **4,** 85–99 (1933).
(12) A. Rollett and R. Petter, *Monatsh.*, **63,** 311–16 (1934).
(13) K. H. Bauer and H. J. Starcke, *Arch. Pharm.*, **272,** 167–71 (1934).
(14) A. Rollett, *Monatsh.*, **58,** 113–17 (1931).
(15) M. Mladenovic, *Bull. soc. chim. roy. Yougoslav.*, **8,** 175–82 (1937).
(16) A. Tschirch, *Arch. Pharm.*, **240,** 263 (1902).
(17) M. Mladenovic, *Monatsh.*, **72,** 350–3 (1939).
(18) M. Mladenovic, *Monatsh.*, **70,** 405–8 (1937).
(19) K. H. Bauer and H. Moll, *Fette u. Seifen*, **44,** 187–8 (1937).
(20) M. Mladenovic, *Monatsh.*, **70,** 276–80 (1937).
(21) M. Mladenovic and I. Berkes, *Monatsh.*, **67,** 36–41 (1935).
(22) P. Casparis and P. Naef, *Pharm. Acta Helv.*, **9,** 19–23 (1934).
(23) L. Ruzicka, R. L. Wakeman, M. Furter, and M. W. Goldberg, *Helv. Chim. Acta*, **15,** 1454–9 (1932).
(24) L. Ruzicka, H. Silbermann, and P. Pieth, *Helv. Chim. Acta*, **15,** 1285–9 (1932).
(25) M. Mladenovic, *Monatsh.*, **61,** 365–8 (1932).

CHAPTER VIII

KAURI

It has been said that even as the English varnish maker made the reputation of kauri, so kauri later made the reputation of the English varnish maker. It has long been the favorite of all varnish makers, as it is easily fused or "run" with drying oils. Its varnishes were long a standard of quality because of their high degree of elasticity and durability. Like congo, kauri imparts depth of gloss to its films.

Fonrobert[1] states, after an investigation of blooming in many different parts of the world, that of all the natural resins kauri is outstanding in its freedom from blooming. Varnishes correctly prepared from kauri did not bloom even in the most humid countries, provided conditions were fairly dry at the time of application and during the drying period.

In common with the other natural resins, kauri varnish films weather in a satisfactory manner and present surfaces requiring but a minimum of preparation for refinishing. Considerable quantities of the lower grades of kauri are used in the manufacture of linoleum and related materials.

Kauri is produced by *Agathis australis*, a conifer, the largest forest tree of the North Island of New Zealand. The resin is a fossil copal, of the same general class as congo and boea. The kauri pine is an evergreen which is believed to reach an age of nearly 3,600 years. The resin is found underground in hilly clay ranges and peat swamps. The trees which produced the kauri resin are no longer in existence, although some minor amounts of the soft type are obtained by tapping living trees. The bulk is fossilized resin of considerable age.

Kauri has the lowest acid value of the fossil copals (60 to 80) and shows solubility in alcohols and ketones as well as in some lacquer solvents. In its original form, it is compatible with a wide range of vegetable, mineral, and petroleum waxes, as well as stearic acid, but the temperatures of combination are such that thermal processing of the kauri takes place. After thermal processing kauri shows compatibility with all animal and vegetable oils. The original resin is compatible with nitrocellulose and ethyl cellulose in specific solvent balances which are detailed in tables contained in the chapter on lacquers. It is incom-

[1] E. Fonrobert, *Paint and Varnish Prod. Mgr.*, April, 1931, p. 36.

patible with cellulose acetate when acetone is employed as a solvent. In its original form, it is incompatible with petroleum asphalt and stearin pitch, but readily miscible by heating with coal-tar pitch and vegetable pitches. After running, it may be blended with all the ordinary varieties of asphalts and pitches, whether these be of vegetable, mineral, or animal origin.

Thermal processing of kauri is not so severe as that required for congo. In ordinary varnish kettle sizes, it is heated to 600°F., in about 1¼ hours, and held at that temperature until oil soluble. The time at the top temperature is about ½ hour. After thermal processing, kauri, like congo, is soluble in a wide range of petroleum and coal-tar solvents, alcohols, esters, terpenic compounds, fatty acids, and vegetable oils. After running, the kauris show softening points of the order of 175 to 200°F., melting points of 250 to 270°F., and acid numbers of the order of 12 to 30. The softening point and melting point of the run resin are functions of the intensity of the thermal processing. Running losses commonly are of the order of 20 to 25 per cent. When formulated on a China wood oil basis, there is no difficulty in preparing satisfactory varnishes of high gloss, adhesion, and durability, which dry in less than 4 hours.

Commercial grades are of three general types: pale, brown, and bush.

Commercial Grades of Kauri

Pale XXXXX	Brown XXX
Pale XXXX	Brown X
Pa'e XXX	Brown No. 1
Pale XX	Brown No. 2
Pale No. 1	Brown No. 3
Pale No. 2	Brown chips
Pale No. 3	Brown dust
Pale chips	Bush bold
Pale dust	Bush chips

The pale designation refers to lack of color. The higher the number of crosses, the closer the approach to white and the greater the freedom from impurities. The cross designation in the brown is similar: the greater the number of crosses, the closer the approach to complete freedom from impurities.

In general, the kauri gums are partially transparent in the pale grades. The number designations are orders of hardness, 1 being harder than 2, and 2 harder than 3. These grades, however, are lower than those designated with the crosses. The chips and dust are size classifica-

tions, as for other resins. Bush gum is virgin material which has fossilized in place on branches of trees and has not been found underground.

It has often been said that the reserves of kauri resin are being rapidly depleted and that complete exhaustion will be seen in the near future. Such statements and beliefs are not substantiated by surveys conducted by the New Zealand Government.[2]

> Taking the total acreage of gum bearing land, both private and Government, that could be profitably rubbled as 300,000 acres, which is a low estimate, it would take 600,000 men 1 year to rubble the whole of the 300,000 acres on the basis of 2 men rubbling 1 acre in 1 year. As the industry under present conditions cannot absorb the output of 3,000 men, it would take that number of diggers 200 years to rubble the 300,000 acres. On a conservative basis, and making due allowance for an increase in demand in the future, it can be taken that the kauri gum bearing lands will provide medium and low grade gums to meet the overseas demand for well over 100 years.

About 800,000 acres of deposits exist, but of this only 300,000 are considered to be profitably workable.

Collection. *Agathis australis* is of very slow growth. It has been estimated that a full-grown tree is from 200 to 300 years old. The trunk at the base may be 20 ft. in diameter and the height may be as much as 160 ft. The lumber of the tree, which is devoid of limbs for its lower 100 ft., is widely used for building purposes and was formerly used to construct the cases in which the resin was exported.

Ages ago the tree grew over a wider area of New Zealand but now is found to any extent only north of Auckland, or in other words, the most northern territory of the North Island of New Zealand. The resin, however, occurs in fair quantities all over the North Island.

In general, the resin-bearing soil extends to a depth of but 5 ft. and rests on a sandstone bottom. In the deeper swamps the resin deposit may be worked considerably beyond this depth. Most of the land is held by the government and worked privately by licensed operators, although a number of rich sections are owned and worked by individuals. In 1925 an act was passed placing control of the production, exporting, and grading of the resin in the hands of the government.

Kauri resins can be classified into two age groups: the fossil variety found under ground, and bush kauri, the hardened sap of the living tree.

In working the deposits, the resin is located by the use of a special steel spear which is 5 to 10 ft. long and about 1/4 sq. in. in cross section.

[2] "New Zealand's Kauri Gum Industry," Australian Commonwealth, 1924.

The tip is tapered to a point and an old spade handle is usually fitted to the top.

The digger bases his trial thrusts in a new location on a survey of the countryside and the contour of the ground. As he presses his spear into the ground he is able to tell if the point encounters resin.

If the extent of the deposit appears worth while, the ground is spaded by hand. A hole is dug about 6 ft. wide and 10 to 15 ft. deep. In wet soil the depth is frequently limited by the amount of water which may accumulate in it. These holes are quite destructive to the landscape and must be filled in if cultivation of the land is to follow.

When working wet locations a pump is in continual operation. The pumps used are quite crude, merely consisting of a wooden plunger within a length of metal piping fitted with a spout. If electric power is available, a small rotary pump is sometimes used.

The use of mechanical apparatus to speed up the digging operation has been tried but proved to be impracticable because of the large logs, limbs, and roots which obstruct progress. In certain deposits, the use of steam shovels for removal of the overburden has proved satisfactory. The logs buried in the ground are quite sizable and the wood is sound lumber. Removal by explosives has not been successful and it has been found necessary to saw the logs into sections and remove them with bullock teams.

The natives of New Zealand, the Maoris, produce very little of the total resin collected. After 1860, European diggers were employed, and in 1890 a number of Slavonic emigrants were engaged in this industry. These men are tall and of splendid physique and are well able to stand the hard work as well as the isolation of the resin-bearing districts. Indians and Chinese laborers have been tried but both found the work too hard and disliked the isolation.

The resin when dug from the ground is covered with earth or clay. Part of this is removed by the diggers at the spot by washing in tubs and sieves or rotary cylinders. The better qualities are also partly scraped with a knife to remove most of the dirt. After this treatment the resin is roughly sorted by the diggers and sold to brokers or direct to the exporters in Auckland. At the exporter's warehouse, the resin is further cleaned and re-sorted to grades.

Resin obtained from the swampy peat moors is known as "swamp" resin, whereas that obtained from the clayey localities is termed "range" resin and is lighter in color. Porous, soft, white resin found with the brown variety is known as "chalk." The white and brown varieties

are roughly separated from each other by immersion in water; the white floats and the brown sinks.

The other variety, bush or bled resin, is obtained by tapping the tree and collecting after about 6 months, or by gathering the hardened resin produced by accidental wounds or normal exudation. Most of the latter is found lodged in the forks of tree branches. Tapping contributes very little to the total supply and is prohibited on government reserves.

Rubbling. With an increased demand for low-grade kauri (principally for the linoleum industry), it became profitable to rework ground previously combed for the bold sizes. The small pieces of resin are known as "chips" and apparently owe their formation to the flattening out and hardening of droplets falling on the swampy ground in a plastic condition. The richest chip areas are found in the tablelands in basins of from ½ to 10 acres.

The chips occur in seams about 2 to 4 ft. below the surface. The resin is obtained by stripping off the top soil and digging out the resin-bearing earth. The earth is removed by putting the earth-resin mixture in a sieve-bottomed tank (about 20 mesh) equipped with an agitator and flushing out with a continuous stream of water. Fibrous vegetable matter is removed by further screening and winnowing. During these latter operations the resin is also graded to size.

Purification by Mechanical Methods. Many attempts have been made to improve the cleaning methods used in the preparation of low grades of kauri resin for market. In 1918 a plant capable of handling a charge of ½ ton was installed at Auckland. The process used was the patented Maclaurin salt-vacuum process in which advantage was taken of differences in the density of resin and soil. In operation, the dirty resin is placed in a cone-shaped tank along with a strong brine solution, agitated by appropriate means, and the air pumped out. Upon cessation of agitation the resin rises to the top while the impurities sink to the bottom. By drawing off separately the upper solution and the lower solution containing suspended dirt a much improved product can be obtained. Both solutions are filtered to recover the brine. The resin is finally washed and dried.

A more extensive flotation plant was erected at Penrose by the Kauri Gum Control Board. The plant has since been dismantled. Diggers' chips from the resin fields, containing anything from 15 to 30 per cent kauri resin in varying small sizes, were first wet with water by rotation in a cylindrical vessel. At the same time a partial cleaning of the resin took place, and the pieces that remained on the surface, freed from a large quantity of mud, were separated at this stage and

added to the cleaned chips. The remainder was passed to a large wooden vat containing a salt solution and slowly stirred. The resin which floated was automatically skimmed from the surface, washed, and dried. The resin and impurities which sank were treated in another vat with a stronger salt solution, and a further separation of resin from debris obtained. The resin was washed free of silt and passed with the previously separated gum into a vertical, continuous, hot-air drier. The dried resin was then passed into a revolving grader and separated into three sizes of resin which emerged over narrow metal slits through which air was drawn. This freed the resin from a large quantity of light fibrous matter, and the cleaned dried resin was collected and packed for export.

The process was continuous, and, it was maintained, purified some of the chips up to a 90 per cent resin content, with a loss of about 5 per cent of the weight of the resin put through. The cost of treatment was estimated at about $20 to $25 per ton.

The products cleaned by this process could not, however, be sold at a price that made refining an economic undertaking. The resin still appeared in grades which varied considerably in resin content, and, although much cleaner than most similar gradings, had an unattractive appearance and were suitable only for linoleum manufacture, the 5 per cent or 10 per cent impurity content excluding them from varnish manufacture.

Solvent Purified Kauri. Purification of kauri was carried out in an experimental solvent extraction plant by the Varnish Products Company (Liquidated) of Auckland in 1927 following the Buchan process.[3] The crude kauri resin (chalk was usually employed) was finely powdered in a hammer mill with water and the slurry pumped into an iron extractor fitted with steam jacket and stirrer. A mixture of benzol (3 parts) with ethyl acetate (1 part) was run into the extractor and the mixture stirred and warmed to 60°C. The mixture was allowed to stand for some 30 minutes, when the clear supernatant solution was drawn off the aqueous layer by means of decanting valves to a tubular evaporator, where the greater part of the solvent was removed and recovered by evaporation with indirect steam. The concentrated resinous solution was then run into an iron vessel and heated to approximately 140°C. under partial vacuum to remove the last traces of solvent. The molten resin was then run out and allowed to cool in shallow trays. Exact figures for the working costs could not be determined during the short time the plant was in operation; it was maintained, however, that 1 ton

[3] British Patent 237,576 (July 23, 1924); U. S. Patent 1,593,964 (July 27, 1926).

of purified resin cost approximately \$8 to \$10 to produce, and the solvent loss amounted to approximately 3 gallons solvent per ton purified resin. Owing to a number of circumstances the process had to be discontinued. The value of the purified product did not warrant its manufacture, and lack of capital forced the company to discontinue its operations at a more or less experimental stage. The solvent mixture employed (benzol and ethyl acetate) did not dissolve the resin completely, only some 40 to 45 per cent of the total resin being taken into solution. The resultant extract did not represent kauri resin, but only those particular constituents of the original resin soluble in such a mixture. A large proportion of the raw material was lost. The purified resin was also very dark because of the high temperature encountered while in contact with iron, and showed physical and chemical properties different from those of kauri resin. The costs of production were too high to enable sales to be made to linoleum factories. Owing to the dark color and abnormal behavior exhibited on running, the purified resin did not find a reception among varnish manufacturers. The product was of good appearance and free from impurities. It appeared that the production of standardized kauri resin along these lines would have more chance of success than by the purely mechanical methods hitherto adopted.

Another solvent purification process was worked out by Hosking,[4] and a few tons produced along commercial operating lines with a benzol-acetone mixture (70 to 30). The crude, washed kauri resin (of about 80 per cent resin content) was passed through crushing rolls and placed in a steam-jacketed extractor together with the solvent. Solution of the resin was obtained at approximately 50°C. by using agitation. Upon solution, stirring was stopped, impurities were allowed to settle, and the clear supernatant solution was drawn off and passed to the evaporator. After evaporating off the solvent under a vacuum by the use of both external and live steam, the resin was solidified on a continuous band drier of the type used in the soap industry. The solvents were reclaimed by passing all vapors through activated carbon adsorbing vessels. The processing cost of a theoretical plant with an annual production of 1,200 tons was calculated at about 4 cents per pound of purified resin delivered overseas.

The samples of purified resin obtained by Hosking with this method were quite clean, usually showing less than 0.5 per cent of insoluble matter. The properties of a number of purified grades are compared in Table VII with those of the original samples.

[4] J. R. Hosking, *New Zealand J. Sci. Tech.*, XVII, No. 1, 369-387 (1935).

TABLE VII

PROPERTIES OF CRUDE AND REFINED KAURI RESINS

	Seeds		Chips		Nubs		Nuts*		No. 1, Light Brown		No. 2, Brown		Chalk	
	Crude	Refined	Crude	Refined	Crude	Refined	Crude	Refined	Crude	Refined	Crude	Refined	Crude	Refined
Moisture (per cent)	4.0	0.6	4.0	0.2	4.4	0.1	7.3	0.1	1.03	2.58	1.88	0.44	28.0	1.30
Insoluble impurities (per cent)	20.9	0.16	4.5	0.02	2.0	0.08	1.7	0.34	0.68	0.05	0.85	0.22	0.20	0.10
Water soluble at 100°C. (per cent)	0.8	0.54	0.50	0.55	0.54	0.32	0.55	0.35	0.35	0.30	0.38	0.36	0.52	0.43
Resin—by difference (per cent)	74.3	98.7	86.5	99.2	93.1	99.5	90.5	99.2	97.9	97.1	96.9	98.9	71.3	98.2
Resin—dry (per cent)	77.4	99.3	90.1	99.4	97.4	99.6	97.6	99.3	98.9	99.6	98.8	99.3	99.3	99.5
Ash (per cent)	4.5	0.09	1.7	0.01	1.0	0.03	0.6	0.06	0.24	0.15	0.31	0.02	0.63	0.04
Melting point (°C.)	..	159–171	..	159–173	..	153–172	..	152–168	..	150–165	..	165–170	..	155–170
Acid value	71	78	74	78	69	74	67	73	..	75	..	78	..	71
Color—Red†	..	29.9	..	29.9	..	29.9	..	20.0	..	3.1	..	3.3	..	1.8
Yellow†	..	5.9	..	4.2	..	2.4	..	2.6	..	0.5	..	0.5	..	0.2

* Not a commercial U. S. grade.

† Lovibond units.

Kauri in Nitrocellulose Lacquers. The use of kauri in nitrocellulose lacquers has been investigated by Spackman[5] who found that such lacquers could be made with solvent mixtures comparable to those used with damar or ester gum. By using correct solvent balances, stable lacquers were obtained which dried to clear films. It was necessary to use a combination of coal-tar solvents and ethyl alcohol along with a portion of medium-boiling alcohols in order to obtain satisfactory films. Alcohol solvents for kauri will tolerate considerable dilution with coal-tar hydrocarbons and somewhat lesser dilution by petroleum solvents without impairment of their solvent power for the resin. In his experiments Spackman used a dried sample of resin and an anhydrous grade of ethyl alcohol.

In a subsequent work[6] the same author studied the solubility of kauri in ethyl alcohol-toluol mixtures and reported them to be superior solvents to ethyl alcohol alone. A mixture of 73.5 parts of ethyl alcohol and 26.5 parts of toluol was recommended.

Physical Constants. A number of physical constants have been determined for kauri.[7]

Electrical resistivity	1.41×10^{17} ohms/cm.^{3} ($\pm 2\frac{1}{2}$ per cent)
Electrical surface resistivity	1.7×10^{14} ohms/cm.^{2} (± 3 per cent)
Dielectric constant	4.7 (± 5 per cent)
Specific heat	0.458 (± 0.5 per cent)

Chemical Composition. The chemical constituents of kauri as found by a number of investigators are given in Table IX.

Hosking[8] has studied the composition of the four types of kauri resin produced: (*a*) resin freshly tapped from the tree, (*b*) tapped resin after exposure to the air for 1½ to 4½ years (bush kauri), (*c*) fossil resin (range resin), and (*d*) fossil resin (swamp resin).

Hosking concluded that the percentage of pinene (the essential oil component) decreases regularly with increasing age of the resin; the optical rotation of the pinene decreasing in the same sense. The range resin showed 6 per cent of a high-boiling fraction of camphor-like odor which was probably fenchyl alcohol formed from the pinene under the influence of water and salts during the examination. The swamp variety contained fenchyl alcohol, dipentene and *d*-α-pinene. The investigation

[5] L. S. Spackman, *New Zealand J. Sci. Tech.*, **12**, 65 (1930).
[6] L. S. Spackman, *New Zealand J. Sci. Tech.*, 13, 301 (1932).
[7] P. W. Burbridge and W. A. Mackay, *New Zealand J. Sci. Tech.*, **9**, 2-3 (1927).
[8] J. R. Hosking, *Rec. trav. chim.*, **48**, No. 6, 622 (1929).

TABLE VIII

Resin	Acid Number	Per Cent Volatile Oil	Per Cent α-Resinic Acids	Per Cent β-Resinic Acids	Per Cent Resene
Fresh	103	8.4	63	19	10
Bush	77	4.9	39	45	9
Range	65	4.0	35	48	9
Swamp	64	0.9	..	..	..

indicated that the amount of α-resinic acids (low-melting acids) decreased with age while the amount of β-resinic acids (high-melting acids) increased. The β-variety appears to be formed from the α-variety, with the change completed in about five years.

TABLE IX

COMPOSITION OF KAURI

Constituent	Formula	Basicity	Melting Point °C.	Per Cent	Remarks
Kaurinic acid (1)	$C_{20}H_{16}O_2$	Mono-	192	1.5	
α-Kaurolic acid (1)	$C_{12}H_{20}O_2$	Mono-	81–83	40–50	Lead salt insoluble in alcohol.
β-Kaurolic acid (1)			85–87		Lead salt soluble in alcohol.
α-Kaurinolic acid (1)	$C_{17}H_{34}O_2$	Mono-	128–130	20–22	Lead salt insoluble in alcohol.
β-Kaurinolic acid (1)			86–89		Lead salt soluble in alcohol.
Kauroresene (1)				12	
"Bitter principle" (1)				0.5–1.0	
α-Resinic acid (2)			121–124		Amount decreases with age.
β-Resinic acid (2)			233–236		Amount increases with age.
Resene (2)					Similar to kauroresene of (1).
Agathic acid (2)	$C_{20}H_{30}O_4$	Di-	203–204		A crystalline acid identical to that found in manila copals. Contains two double bonds of equal reactivity.

(1) A. Tschirch and B. Niederstadt, *Arch. Pharm.*, **239,** 145 (1901).
(2) J. R. Hosking, *Rec. trav. chim.*, **48,** No. 6, 622 (1929); L. Ruzicka and J. R. Hosking, *Ann.*, **469,** 147 (1929).

Utilization of Waste Kauri Wood. Attempts[9] have been made to utilize waste kauri wood as a source of paper pulp. The pulps furnished paper of excellent strength and quality, with fibers longer and coarser

[9] *New Zealand J. Sci. Tech.*, **9,** 4 (1927).

than those from commercial coniferous wood. Although they did not bleach well with the same amount of bleach used for ordinary spruce pulp, a pale cream-colored paper was produced. Yields as high as 47 per cent of dry pulp were obtained.

SUPPLEMENTARY REFERENCES

W. E. LANGGUTH, "Kauri Gum," *Paint, Oil Chem. Rev.*, **78**, No. 10, 6-7 (1924).
F. FRITZ, "The Production of Kauri Copal," *Farben-Ztg.*, **31**, 156-8, 220-2 (1925).
H. WOLFF, "Examination of Kauri Dust," *Farben-Ztg.*, **31**, 2609-11 (1926).
E. STOCK, "Refined New Zealand Kauri Copal," *Farben-Ztg.*, **41**, 182-3 (1936).

CHAPTER IX

THE MANILAS

The Manila resins are the exudations from *Agathis* trees of the botanical family *Araucariaceae*. Some controversy exists as to the exact species. Foxworthy[1] traces all manilas to the single tree, *Agathis alba*. Van de Koppel, when chief of the Forestry Service of the Netherlands East Indies Government, studied the economically valuable flora of the Netherlands Indies for many years and is of the opinion that other similar trees may also supply resin. It has been definitely established that this is true of pontianak. The recent work of Jakobs[2] on the relationship of the melengkets and lobas would appear to substantiate van de Koppel's contention. However, at the present time, with the exception of pontianak, the bulk of commercial manila is the product of *Agathis alba*.

The agathis trees are found throughout the Philippine Islands and the Netherlands East Indies with the exception of Java. The shorea and hopea trees, from which damar is produced, occur mainly in the western portion of the East Indian archipelago. Proceeding eastward, the damar-producing trees decrease in number while the agathis trees become more numerous.

The production of Manila copal originated in the Philippine Islands, where both the tree and resin are known as almaciga. The name "manila" was taken from the port at which the resin entered commerce. At the present time, however, the bulk of Manila copal comes from the East Indies, where the resin is systematically produced under supervision by the Dutch Government.

Borneo, Celebes, the Moluccas, the Philippines and New Guinea produce most of the world's supply of Manila copal. Agathis trees exist on the Malay peninsula also. Little copal is collected, as the trees are not easily accessible. The exuded resin (syrup copal) does not harden so rapidly as that obtained in the East Indies.

Agathis alba is a typical conifer with a straight smooth trunk, which grows to a height of 200 ft. It is nearly as tall as the giant kauri pine of

[1] F. W. Foxworthy, *Philippine J. Sci.*, 52, 173 (1910).

[2] H. Jakobs, *Tectona*, 33, January, 1940.

New Zealand, but is smaller in diameter. Some of the largest specimens with a diameter of 7 ft. have been estimated to be 500 years old. Typical trees are shown in Fig. 16.

The manilas are obtained by deliberate tapping of the tree and from accidental wounds. The method of tapping is considerably different

Courtesy C. van de Koppel

FIG. 16. *Agathis alba,* about 150 ft. high, Celebes.

from that of damar, as the resin from the agathis trees is obtained from the bark only. In tapping, the bark is cut off horizontally down to the wood and the wood underneath is then cleaned to provide a surface upon which the resin collects. After every collection of resin a thin slice of bark is cut off to provide a fresh opening for the resin ducts. Average production is 26 to 27 pounds a year per tree. Minimum diame-

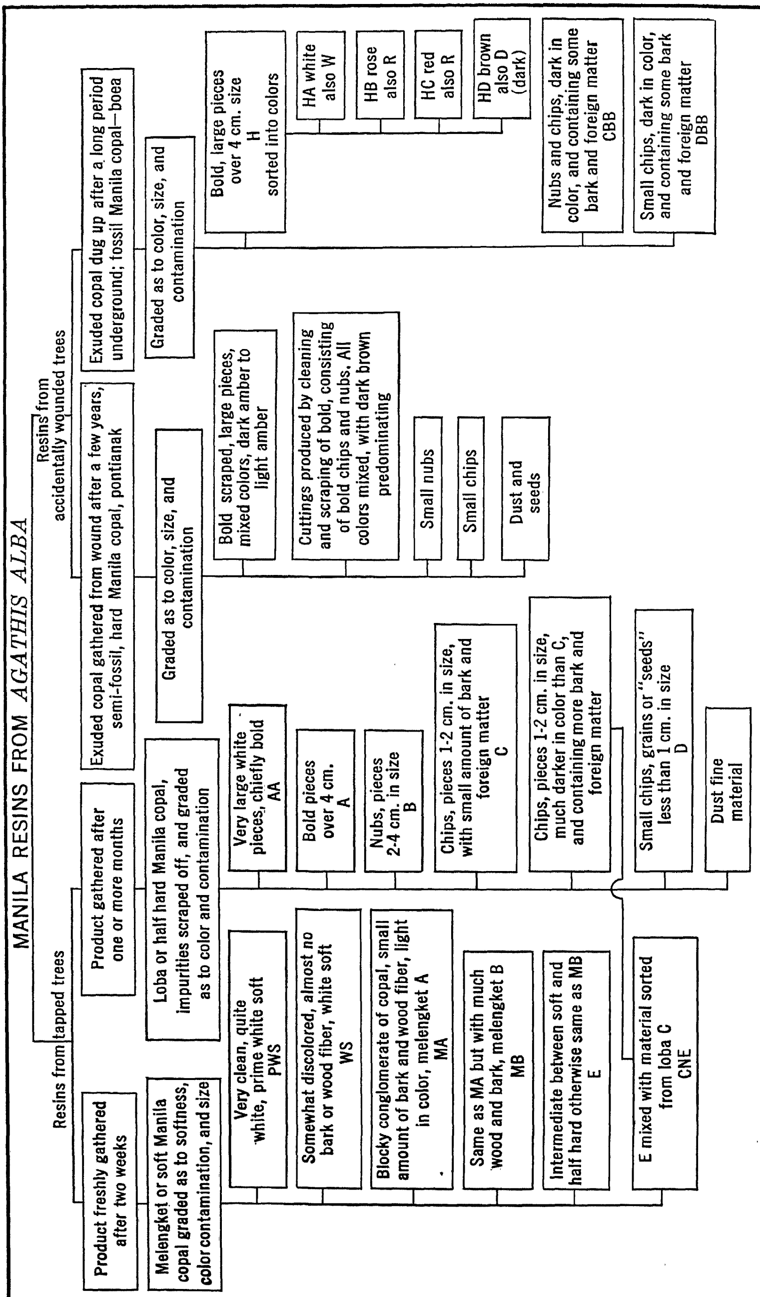


FIG. 17. Origin and grades of Manila resins.

ter of trees for tapping, and size and number of tap wounds are regulated by law.

Manila resins are divided into classes according to the age of the resin. The relationship between the various classes is shown in Fig. 17.

The manilas are also designated as Macassar, Singapore, and Philippine manilas according to the point at which they enter commerce. The commercially important grades marketed in this country are listed in the following table:

Macassar Manila
- Manila WS pale soft
- Manila MA soft blocky
- Manila MB soft blocky
- Manila loba A bold pale
- Manila loba B bold pale nubs
- Manila loba C bold pale chips
- Manila loba D small pale chips
- Manila loba DK dark chips
- Manila loba FAX pale nubs
- Manila loba CNE dark nubs
- Manila loba dust
- Manila CBB medium pale nubs
- Manila DBB pale chips

Boea
- Hard bold white
- Hard bold amber
- Hard bold dark

Philippine Manila
- Manila extra bold pale scraped
- Manila bold pale
- Manila bold extra pale sorts
- Manila bold pale chips
- Manila bold small chips
- Manila bold amber sorts
- Manila seeds and dust

Singapore Manila
- White split chips
- Singapore manila dust

Pontianak
- Pontianak bold scraped
- Pontianak mixed bold
- Pontianak cuttings
- Pontianak nubs
- Pontianak chips

The softest grades, gathered from three or four weeks down to one week after tapping, and called melengket by the natives, are exported from the Netherlands Indies in four qualities. The finest grade, PWS (prime white soft), is nearly water-white in color and almost entirely free from impurities of any sort. WS (white soft) is very clean and quite light in color. MA (or melengket A) may contain some bark and wood fiber. The latter grades are the most used in the United States. MB (or melengket B) may contain considerable amounts of woody impurities. Currently it is not much in demand in the United States but finds outlets abroad. These soft grades arrive on the market as blocky lumps, clear and free from any surface crust. A slightly older and harder grade is called E and is marketed in admixture with the C grade of the loba type of manila as loba CNE.

Half-hard manila, or manila loba, is the designation of material gathered from one to three months or more after tapping. The resin has

become hard enough so that the pieces do not block together as does the soft manila. It is scraped free of surface impurities and graded according to size of piece, from A (over 4 centimeters) to D (less than 1 centimeter) and dust. The FAX pale nubs are cleaner and lighter than the

Courtesy C. van de Koppel

FIG. 18. Tapping and collecting loba from *Agathis alba.*

DK or small dark chips, which are quite dirty, or the CNE which contains considerable crusty resin.

These are Netherlands Indies gradings. Singapore copal, which originates in Borneo, is of the same type. Philippine manila is also resin of about the same age; it is sorted according to both color and size of piece.

The fossil grade of manila is derived from the Netherlands Indies

and is known as boea or hard manila. The light-colored variety is found where it has exuded in the crotches of trees still standing. The collection of white boea is an arduous task as the resin occurs at great heights.

Courtesy C. van de Koppel

FIG. 19. Manila resin exudation.

The natives ascend the tree with the aid of wooden pegs driven into the trunk. The rattan used in the collection of damar is not usually employed.

The amber and dark grades are found buried in the ground, often in masses so huge that the botanists are completely at a loss to account for their formation. Manila CBB and manila DBB are grades consisting of a mixture of boea with loba. The excellence of boea as a varnish

resin is outstanding, but it is the only one of these grades which is subject to diminishing supply. It is to be hoped that some treatment of the more recent Manila resins may be devised to obtain from them a product with the same characteristics.

Pontianak is a semi-fossil copal which is a member of the manila class. It originates in Borneo, whereas boea comes chiefly from Celebes and other parts of the Netherlands Indies. Pontianak is the product of *Agathis borneënsis* and differs therein from boea which is obtained from *Agathis alba.* Although it is alcohol soluble and finds application in spirit varnishes, pontianak is commonly thought of as an oil-varnish resin. It behaves more like kauri in the varnish kettle, but otherwise its properties and the properties of its varnishes make it almost indistinguishable from boea. The varnish resin pontianak should not be confused with the rubber type of material known as jelutong or gutta siak, which is often termed pontianak in the rubber trade.

The Manila resins are imported in containers of local origin, in weights which have become standard by long usage. With the exception of pontianak bold, which is shipped in cases of 224 pounds, basket bags or bags containing 160 pounds are used.

The chemical composition of the Manila copals has been the subject of a number of investigations, the more important results of which are given in Table X.

The complex nature of the natural resins and the ease with which individual constituents undergo chemical changes make the chemical examination of the resins a difficult problem. The procedure usually consists of some combination of fractional extractions, precipitations, and crystallizations. Where isomeric acids are to be dealt with, separation is usually obtained through fractional crystallization of metal salts of the acids, the acids being subsequently regenerated by treatment with mineral acids and purified by recrystallization from an organic solvent. The method employed by Tschirch and Koch is typical of the many modifications which have been used. The method, as briefly outlined, follows.

Mancopalinic and mancopalenic acids are separated from the ether solution of the resin by extraction with ammonium carbonate. The extracted resin acids are precipitated with hydrochloric acid. Mancopalinic acid is obtained by crystallization from a methyl and ethyl alcohol solution followed by recrystallization from dilute alcohol. The mancopalenic acid is precipitated from alcohol solution as the lead salt by addition of lead acetate. The precipitate is treated with alcohol which has been acidified with sulfuric acid. The lead sulfate precipitate obtained is removed by filtration. The resin

TABLE X

Composition of Manila

Constituent	Formula	Basicity	Melting Point °C.	Per Cent	Remarks
Mancopalinic acid (1)	$C_8H_{12}O_2$	Mono-	175	4	A soft reddish yellow resin soluble in alcohol.
Mancopalenic acid (1)	$C_8H_{14}O_2$	Mono-	100–105		
α-Mancopalolic acid (1)	$C_{10}H_{18}O_2$	Mono-	85– 90	75	
β-Mancopalolic acid (1)		Mono-	85– 88		
Mancopalresene (1)	$C_{20}H_{32}O$		80– 85	12	
Essential oil (1)			B.P. 165–170	6	
Water (1)				2	
Succinic acid and impurities (1)				1	
α-Mancopalolic acid (1)	$C_{10}H_{18}O_2$	Mono-	88– 92	80	A hard, pale yellow resin partially soluble in alcohol obtained from Gorontalo in the Celebes and marked "M.C., hard shiny."
β-Mancopalolic acid (1)		Mono-	86– 90		
Mancopalresene (1)	$C_{20}H_{32}O$		80– 85	12	
Essential oil (1)			B.P. 165–170	5	
Water (1)				2	
Succinic acid and impurities (1)				1	
Mancopalinic acid	$C_{10}H_{15}O_2$ (2) $C_{22}H_{34}O_4$ (2) $C_{32}H_{50}O_4$ (2)	Mono- Mono-	185–187		Richmond's results are in fair agreement with those of Tschirch and Koch but he did not confirm their detailed account of the resin acids. He enumerates the difficulties encountered in the chemical examination of the resin acids.
An amorphous acid	$C_{15}H_{24}O$ (3) or $C_{16}H_{18}O_2$ $C_{23}H_{34}O_4$ (3) $C_{40}H_{60}O_4$ (3)	Mono- Di- Di-			The second acid is apparently the same as Richmond's $C_{22}H_{34}O_4$ but is reported dibasic while Richmond's acid is reported as monobasic. This group also reported work on the distillation and hydrogenation of the acidic constituents.
An acid	$C_{20}H_{32}O_4$ (4) or $C_{19}H_{30}O_2$				Scheiber believed Tschirch and Koch's α- and β-maneopalolic acid as well as Richmond's acid to be impure forms of this acid.
Copal dicarboxylic acid	$C_{20}H_{32}O_4$ (5) When heated above its melting point loses CO_2 and yields $C_{19}H_{32}O_2$ (5)	Di- Mono-	 60		These investigators also repeated Tschirch and Koch's work on a soft alcohol-soluble manila but could not obtain definite results.
Agathic dicarboxylic acid	$C_{20}H_{30}O_4$ (6) loses CO_2 $\downarrow$ on heating	Di-	203–204		Using the method of Horrman and Kroll, Ruzicka and Hosking obtained this acid from the ether-soluble acids of kauri and hard and soft Manila copal. They considered the various dibasic acids of other investigators to be impure forms of this acid. Agathic acid was found to contain two double bonds of equal reactivity.
Noragathic acid	$C_{19}H_{30}O_2$ (6)	Mono-	B.P. 195–197 (0.9 mm.)		

(1) A. Tschirch and M. Koch, *Arch. Pharm.*, **240**, [3] 202 (1902).
(2) G. F. Richmond, *Philippine J. Sci.*, **5** (A), 177 (1910).
(3) L. Ruzicka, R. Steiger, and H. Schinz, *Helv. Chim. Acta*, **9**, 962 (1926)
(4) J. Scheiber, *Ann.*, **453**, 52 (1927).
(5) P. Horrman and B. Kroll, *Arch Pharm.*, **265**, 214 (1927).
(6) L. Ruzicka and J. R. Hosking, *Ann.*, **469**, 147 (1929).

acid is precipitated from the alcoholic filtrate with hydrochloric acid, filtered, and washed. The resin acid is dissolved in ether and agitated with a 1 per cent aqueous solution of ammonium carbonate. The extracted material is then reprecipitated with hydrochloric acid, washed, and dried.

The isomeric mancopalolic acids are separated from the original ether solution of the resin by extraction with sodium carbonate. Treatment of the extracted material with alcoholic lead acetate yields an insoluble lead salt of α-mancopalolic acid and a soluble lead salt of the β-isomer. The solution is then filtered, the insoluble salt washed with alcohol and treated with alcohol which has been acidified with sulfuric acid. The precipitated lead sulfate is filtered off and the filtrate added to a dilute hydrochloric acid solution. The precipitated α-mancopalolic acid is filtered off, washed, redissolved in ether, extracted with sodium carbonate, and reprecipitated.

The filtrate containing the soluble lead salt of the β-isomer is treated with sulfuric acid to remove the lead and then purified in the same manner as the α-acid.

The original ether solution remaining from the ammonium carbonate and sodium carbonate extractions now contains only the essential oil and mancopalresene. The essential oil is removed by steam distillation and the resene purified by reprecipitation. The properties and constants of the purified materials are determined by ordinary methods.

Tedious and painstaking procedures are necessary for successful isolation of the resin constituents. Separation of the resin acids from the original ether solution required fifty ammonium carbonate extractions and one hundred and ten sodium carbonate extractions.

Richmond followed the method of Tschirch and also used a modification of his own in which the resin acids are precipitated from alcohol solution by the addition of alcoholic potassium hydroxide.

Scheiber obtained his acid by precipitation from sodium hydroxide solution with hydrochloric acid, followed by ammonium carbonate extraction and recrystallization.

Horrmann and Kroll in their method examined portions of resin obtained by fractional extraction with organic solvents and isolated the constituents by ammonium carbonate, sodium carbonate, and sodium hydroxide treatment of the extract. The same method was used by Ruzicka and Hosking in the isolation of agathic acid and the determination of its formula.[3] The relationship of agathic acid to pimanthrene and trimethylnaphthalene and the structure of pimanthrene were also studied.[4] Reference should be made to the original article.

[3] L. Ruzicka and J. R. Hosking, *Helv. Chim. Acta* **14**, 203 (1931).

[4] L. Ruzicka, G. R. B. de Greef, and J. R. Hosking, *Helv. Chim. Acta* **14**, 233, (1931).

The manilas present the widest range of variations in physical and chemical properties of any one class of natural resins. The specific gravity of Manila resins varies from 1.06 to 1.08. Other properties vary according to the origin and age of the particular shipment examined, but the approximate limits of these variations may be defined as shown in Table XI.

TABLE XI

Resin	Melting Point °C.*	Direct Acid Number	Indirect Acid Number	Saponification Number	Iodine Number
Soft and half-hard manilas	115–135	125–150	140–165	160–190	120–130
Boea	130–135	125–150	145–150	145–175	110–135

* Melting point determined by the mercury method.

The acid and saponification values for Philippine manila run about ten points lower than the corresponding values for half-hard manilas from the Netherlands Indies. These same values for pontianak are lower than those for boea by about the same amount.

Manila resins are characterized by alcohol solubility. In the scale of hardness they occupy a wide range beginning with the soft melengkets and followed by the half-hard lobas and the hard pontianaks and boeas. With the exception of the brown fossil variety found buried in the earth, Manila copal is light in color; commercial grades vary from yellow to almost water-white. It is quite transparent and is not sticky to the touch.

Although compatible with a wide range of materials used for the production of surface coatings, the manilas must be thermally processed in order to render them oil soluble. Also, as might be expected from their relatively high acid values, the manilas can be esterified with glycerol or other polyhydric alcohols. Other chemical alterations are also possible which produce resinous materials of markedly differing characteristics when compared to the original copal. The chemical reactions involved and the products obtained are thoroughly discussed in later chapters.

The major applications of manilas are in oil and spirit varnishes and paints, for which they are adapted by their light color and wide range of solubility and hardness. Boea is employed in the preparation of oil

varnishes, to which the resin imparts hardness and durability. Pontianak finds use in oil varnishes, to which it imparts characteristics similar to those of boea, and also finds applications as a spirit-varnish resin. The lobas and melengkets are seldom used in oil varnishes, as they are somewhat more difficult to render oil soluble, but are extensively used in spirit varnishes for a multitude of purposes and in the production of lacquers and spirit-type paints.

Since soft and half-hard Manila copals have a hardness equal to that of shellac, although their spirit-varnish films are somewhat more brittle, they are frequently used as the basic material in the preparation of shellac substitutes. The solubility of these resins in aqueous alkaline solutions has led to their use as sizing materials and in a variety of other applications for which water-dispersible resins are required. The manilas also have numerous other miscellaneous applications, among which are the preparation of such materials as plastics, japans, driers, linoleum, oilcloth, waterproofing compositions, polishes, printing inks, and adhesives.

CHAPTER X

MASTIC

Commercial gum mastic is the resinous exudation of *Pistacia lentiscus*, a tree belonging to the botanical family *Anacardiaceae*. A number of other *Pistacia* trees produce resins. These materials, however, are either used locally or marketed in Europe as inferior grades or substitutes for true mastic.

The tree from which mastic is produced is widely disseminated throughout the western portion of the Mediterranean coastal region. The collection of resin, however, is largely limited to the Greek island of Chios near the coast of Turkey, where the species is cultivated for this purpose.

The *Pistacia lentiscus* is a wide-leafed, shrubby tree usually attaining a height of about 10 ft. A more common variety is known which does not produce a satisfactory resin. Mastic resembles natural amber in that it is not secreted as the result of injury to the trees but is a spontaneous exudation which under normal circumstances accumulates and hardens as drops or globules upon the twigs and branches. The yield obtained is small, however. Since the flow of resin is stimulated by wounding, the tree is tapped for commercial production.

The tapping consists of a series of relatively closely spaced, narrow, vertical incisions extending from the base of the tree to the branches. The incisions are not deep, as it is only necessary to remove the bark and very slightly wound the tree. The resin exudes and hardens in these cuts in the form of drops or tears, part of which remains attached to the tree while the balance becomes detached and falls to the ground. Two commercial grades of resin are obtained, the first and cleaner directly from both the incisions and twigs of the tree and the second contaminated more or less by falling to the earth. The purity of the second grade is improved by such methods as moistening and firmly packing the earth upon which the resin falls, or placing clean sand or flagstones about the base of the tree.

The product from the tapped tree becomes gradually poorer. Satisfactory resin is usually produced for about only four years. The harvesting period extends from July to October and the average production is from 10 to 12 lb. per year per tree. The product is exported in cases weighing from 110 to 140 lb.

Tschirch and Reutter[1] studied the composition of Chios mastic by the usual method (extraction of the ether solution with 1 per cent ammonium carbonate, sodium carbonate, and caustic solutions). The results of their investigation are given in Table XII.

TABLE XII

CHEMICAL COMPOSITION OF MASTIC

Constituent	Formula	Basicity	Melting Point °C.	Per Cent
α-Masticinic acid	$C_{23}H_{36}O_4$	Mono-	90–91	4
β-Masticinic acid	$C_{23}H_{36}O_4$	Mono-	89–90.5	
Masticolic acid	$C_{23}H_{36}O_4$	Mono-	201	0.5
α-Masticonic acid	$C_{32}H_{48}O_4$	Mono-	96–96.5	20
β-Masticonic acid	$C_{32}H_{48}O_4$	Mono-	91–92	20
α-Masticoresene	$C_{35}H_{36}O_4$		74–75	30
β-Masticoresene				20
Essential oil				2
Bitter principle, impurities, etc.				5.5

The commercial resin is usually a pale yellowish or greenish material, in the form of transparent tears or sorts. (Fluckiger attributes the greenish tinge to chlorophyll.) The freshly fractured surface has a glassy luster. Mastic is a relatively soft resin, soluble in alcohol and aryl hydrocarbons but insoluble in aliphatic hydrocarbons. Its melting point and acid value are both low.

Mastic is compatible with a wide range of vegetable oils and with cellulose derivatives such as nitrocellulose and ethyl cellulose, but shows slight incompatibility with cellulose acetate. It is readily miscible by heating with asphalts and pitches of a wide variety.

The resin is primarily used in applications requiring a very pale and transparent varnish. In spirit varnishes mastic has found favor with artists for many centuries as a protective coating for fine paintings in oil, water color and other media. It possesses an advantage for this purpose over other resinous materials since the varnish can be readily removed without injury to the painted surface beneath. The elasticity of mastic varnishes is quite high and plasticizing is not generally necessary. In the United States mastic finds miscellaneous uses in spirit varnishes, lacquers, and adhesives, as well as in some lithographic processes, and as a constituent of incense.

[1] A. Tschirch and L. Reutter, *Arch. Pharm.*, **104**, 242 (1904).

CHAPTER XI

SANDARAC

Sandarac is obtained from *Tetraclinis articulata* trees of the *Coniferae* family. Commercial sandarac originates in northern Africa. A smaller amount of sandarac comes from Australia where the resin is attributed to members of the species *Callitris* and is reported to be identical with the African resin.

Tetraclinis articulata is a small tree which is cultivated on the southern slopes of the Atlas Mountains in Algeria and Morocco. The resin enters commerce from the port of Mogador in Morocco and is frequently termed "Mogador sandarac." Collection of the resin is similar to that of mastic, incisions being made to stimulate the flow of resin. The exudation is transparent but gradually becomes more opaque owing to oxidation and evaporation from the surface of the globule. As in the case of mastic, there are two grades, depending upon whether the resin is collected from the tree or from the ground. The resin is exported in casks or bags of 300 pounds.

Sandarac is pale, brittle, and transparent. The pieces may be covered by an opaque crust. Its softening point ranges from 100 to 130°C. and its melting point from 135 to 150°C. In acid value and saponification value it is comparable to the manilas, the ranges being 117 to 155 and 145 to 157 respectively. It is soluble in alcohols, but insoluble in both aryl and aliphatic hydrocarbons.

Sandarac is readily compatible with ethyl cellulose, but shows slight incompatibility with nitrocellulose in Cellosolve and with cellulose acetate in dioxane. It is miscible by heating with vegetable and coal-tar pitches, but is incompatible with petroleum asphalt and stearin pitches. Sandarac is incompatible, under the normal methods of making the test, with varnish oils.

In the past, sandarac found favor in lacquers and spirit varnishes for coating paper and finishing wood and metal. One of its largest applications was as a primer for metal surfaces to which it provides a high degree of adhesion. Sandarac was also used in bookbinders' and spirit varnishes and lacquers for photographic work, and as a constituent of incense and dental cements. It gives pale, hard spirit varnishes of high luster and is particularly adapted to the finishing of metal objects. Many of its uses are in combination with mastic and elemi.

With mastic, sandarac has been used for many years in the preservation of fine paintings.

Several investigators have studied the chemical composition of sandarac. Although the results tabulated in Table XIII are not in complete agreement, they permit an approximation of the composition of the resin.

TABLE XIII

CHEMICAL COMPOSITION OF SANDARAC

Constituent	Formula	Per Cent	Remarks
"Resin A" (1) "Acid B" (1) "Acid C" (1)	$C_{40}H_{31}O_5$ $C_{40}H_{31}O_6$		No detailed examination of these constituents was made other than to determine the empirical formulae.
Three acids	$C_{40}H_{62}O_5$ (2) $C_{40}H_{62}O_6$ (2) $C_{40}H_{60}O_6$ (2)		
Sandaracolic acid	$C_{45}H_{66}O_7$ (3) or $C_{43}H_{61}O_3(OH)(OCH_3)$ COOH	85	This material is monobasic, with a melting point of 140°C.
Callitrolic acid	$C_{65}H_{84}O_8$ (3)	10	
Essential oil and bitter principle (3)		2.84	
Water (3)		0.56	
Ash (3)		0.1	
Impurities (3)		1.5	
i-Pimaric acid	$C_{20}H_{30}O_2$ (4) $C_{30}H_{48}O_5$ (4)		Henry pointed out that the formula $C_{65}H_{84}O_5$ was inconsistent with the data obtained by Tschirch and Balzer for callitrolic acid. $C_{62}H_{84}O_5$ is nearer to the correct value.
Sandaracopimaric acid	$C_{20}H_{30}O_2$ (5)		
Sandaracinolic acid	$C_{24}H_{36}O_2$ (5)		
Sandaracic acid	$C_{22}H_{34}O_3$ (5)		
	$C_{20}H_{30}O_2$ (6)	0.7	
Neutral oil—*d*-α-pinene *d*-limonene di- or tricyclic terpenic compounds and their derivatives (7)		8	

(1) J. F. W. Johnson, *Phil. Trans.*, **129**, 293 (1839).
(2) Schützenberger, "*Traité de chim. générale*," VI, 103.
(3) A. Tschirch and F. Balzer, *Arch. Pharm.*, **235**, 289 (1896).
(4) T. A. Henry, *Trans. Chem. Soc.*, **79**, 1144 (1901).
(5) A. Tschirch and M. Wolff, *Arch. Pharm.*, **244**, 684 (1906).
(6) F. Balas and J. Brzak, *Coll. Czech. Chem. Comm.*, **1**, 306 (1929).
(7) F. Balas and Z. Pejova, *Coll. Czech. Chem. Comm.*, **2**, 424 (1930).

CHAPTER XII

PHYSICAL AND CHEMICAL PROPERTIES

As the industries in which the natural resins serve as raw materials have grown older and have broadened in scope, and as the number of basic substances available to these industries has increased, it has become more necessary that the consumers possess a broad knowledge of their characteristics in order to apply them to their best advantage. The earlier natural resin literature has not been conducive to such a knowledge. Little has been published in reference to the characteristics of the commercial resin grades and what information has been made available has been obtained from such a variety of sources and by such a variety of methods that it is of little value even when used for purposes of comparison among the naturals themselves.

In Table XIV the constants of all the present grades of natural resins are given, as determined by methods described in Chapter XXVI.

Scratch Hardness. In general, the fossil resins and the copals are harder than the damars, although the classes cross each other in the softest copals and the hardest damars. The usual order of hardness is as follows:

1. Congo
2. Kauri
3. Boea
4. Pontianak
5. Accroides
6. Loba
7. Pale east india
8. Black east india
9. Batu
10. Manila melengkets
11. Damar
12. Sandarac
13. Mastic
14. Elemi

Bulking Value. In the preparation of resin solutions it is desirable to know the concentration of a filtered solution obtained by dissolving a specified weight of resin in a specified weight of solvent, as well as the weight of resin which must be dissolved per gallon of solvent to produce a clear resin solution of specified concentration. In both it is useful to know the volume of solution produced and also the weight per gallon or specific gravity of the resulting solution. It is necessary that the bulking value of the resin and its insoluble content be known, and also the specific gravity of the solvent. From these values a chart can be constructed for any resin in any solvent (covering the entire

TABLE XIV. PHYSICAL AND CHEMICAL PROPERTIES OF

Name of Resin	Refractive Index	Softening Point		Melting Point	
		°C.	°F.	°C.	°F.
Pale east india macassar					
Bold—hiroe	1.543	101–112	214–234	127–156	261–313
Nubs—hiroe	1.542	103–110	217–230	127–143	261–289
Chips—hiroe	1.540	105–120	221–248	133–137	271–279
Dust—hiroe		116–122	241–252	140–156	284–313
Pale east india singapore					
Bold	1.541	109–128	228–262	147–156	297–313
Nubs	1.541	110–117	230–243	153–163	307–325
Chips	1.540	110–122	230–252	138–149	280–300
Dust		114	237	150	302
Batu east india					
Scraped	1.538	111–132	232–270	168–180	334–356
Unscraped		124	255	169	336
Nubs and chips		127	261	160	320
Dust		131	268	165	329
Black east india					
Bold scraped	1.541	114–125	237–257	160–164	320–327
Bold unscraped		120	248	159	318
Nubs and chips		114	237	161	322
Batavia damar					
A/E standard	1.535	70–76	158–169	102–107	216–225
A/D mixed		75	167	110	230
A	1.535	67–75	153–167	99–112	210–233
B	1.535	70–75	158–167	96–100	205–212
C	1.535	70–75	158–167	99–107	210–225
D	1.535	74–80	165–176	99–109	210–228
E	1.536	74–75	165–167	99–102	210–216
F		70	158	108	226
Dust	1.536	70–76	158–169	102–114	216–237
Singapore damar					
No. 1	1.538	67	153	115	239
No. 2		71	160	114	237
No. 3		75	167	115	239
Seeds		73	163	115	239
Dust		72	162	114	237
Manila (macassar)					
WS pale soft	1.526	80–88	176–190	115–128	239–262
MA soft blocky	1.526	77–88	171–190	121	250
Loba A bold pale		82	180	117	243
Loba B bold pale nubs	1.539	73–90	163–194	120–124	248–255
Loba C bold pale chips	1.540	81–88	178–190	114–123	237–253
Loba D small pale chips	1.539	83–89	181–192	114–127	237–261
Loba DK dark chips	1.538	71–89	160–192	114–130	237–266
Loba CNE dark nubs		79–90	174–194	116–127	241–261
Loba dust		78–91	172–196	116–125	241–257
CBB medium pale nubs	1.538	82–90	180–194	119–130	246–266
DBB pale chips	1.538	78–88	172–190	120–129	248–264
Singapore manila					
White split chips		94	201	126	259

Commercial Grades of Natural Resins*

Specific Gravity	Direct Acid Number	Indirect Acid Number	Saponification Number	Iodine Number	Solubility Type	Insolubility Type
1.03–1.04 1.03–1.05 1.03–1.05	16–21 20–23 24–30 28–35	23–30 28–32 37–43 46–69	40 47 54 65	90–115 66–85 82–84 68–80	Aryl hydrocarbons, hydrogenated aliphatic hydrocarbons	Alcohols, esters, ketones
1.04–1.05 1.04 1.03–1.06	20–27 19–25 23–31 27	37–38 28–35 33–44 43	35 33 40	83–85 79–81 73–87 81	Aryl hydrocarbons, hydrogenated aliphatic hydrocarbons	Alcohols, esters, ketones
1.00–1.05 1.00–1.02 1.02–1.03	18–20 28 32 46	33 40 41 50	33 47 51 56	81 77 71 64	Aryl hydrocarbons, hydrogenated aliphatic hydrocarbons	Alcohols, esters, ethers, ketones, terpenes
1.04 1.04 1.04	20 25 28	34–36 31 37	27–37 39 46	83 81 81	Aryl hydrocarbons, hydrogenated aliphatic hydrocarbons	Alcohols, esters, ethers, ketones, terpenes
1.04–1.06 1.06	25–31 27	31–34 34	29–39 34	95–112 109	Aryl and aliphatic hydrocarbons, terpenes	Alcohols, esters
1.04–1.06 1.04–1.06 1.03–1.06 1.04–1.06 1.04–1.06	24–30 22–32 24–32 25–33 27–33	26–31 24–31 24–37 24–33 33–39	30–33 30–31 27–35 33–38 44–50	96–127 95–118 96–118 89–111 79–103		
	33 32–33	38 37–44	48 46–50	97 64–93		
1.04–1.05 1.05 1.06 1.06	17 32 28 28 32	26 41 40 39 45	36–39 33 40 42 43	103–123 104 95 91 84	Aryl and aliphatic hydrocarbons, terpenes	Alcohols, esters
1.06–1.07 1.06–1.07	135–137 127–134	150–165 149–165	170–190 158–190	118–124 121–126	Alcohols, esters, ketones	Aryl and aliphatic hydrocarbons
1.08 1.07–1.08 1.07–1.08 1.07–1.08 1.07 1.07	149 136–139 139–141 127–131 127–131 125–133 110–131	162 147–162 152–155 151–164 146–161 144–163 134–159	176 160–170 160–170 160–180 165–180 168–190 160–177	122 116–124 119–125 114–115 107–111 104–130 68–87	Alcohols and ketones	Aryl and aliphatic hydrocarbons
1.06–1.08 1.06–1.07	134–141 135–143	152–164 154–163	176–190 170–179	114–120 112–113		
1.07	120	139	144	125	Alcohols and ketones	Aryl and aliphatic hydrocarbons

TABLE XIV

Name of Resin	Refractive Index	Softening Point °C.	Softening Point °F.	Melting Point °C.	Melting Point °F.
Manila (Philippine) spirit soluble					
Extra bold pale scraped		86	187	123	253
Bold pale		89	192	129	264
Bold extra pale sorts		96	205	128	262
Bold pale chips		91	196	129	264
Pale small chips		93	199	130	266
Bold amber sorts		103	217	128	262
Seeds and dust		110	230	132	270
Pontianak					
Bold scraped		87–135	189–275	135–161	275–322
Mixed bold		95	203	126	259
Cuttings		91	196	138	280
Nubs	1.540	99–135	210–275	136–169	277–336
Chips		82–132	180–270	136–156	277–313
Boea manila					
Hard bold white		79	174	130	266
Hard bold amber	1.540	80	176	131	268
Hard bold dark	1.539	80	176	132	270
Various					
Gum elemi		Plastic			
Gum mastic		55	131	76	168
Red gum coarse (accroides)		75	167	110–128	230–262
Red gum powdered (accroides)		85	185	134	273
Sandarac	1.545	100–130	212–266	135–150	725–302
Kauri					
Pale XXXXX		105	221	130	266
Pale XXX		110	230	129	264
Pale XX		105	221	130	266
Pale No. 1		90	194	128	262
Pale No. 2		105	221	127	261
Pale No. 3	1.546	130	266	134	273
Pale chips	1.546	125	257	133	271
Pale dust		126	259	131	268
Brown XXX		120	248	128	262
Brown X		125	257	141	285
Brown No. 1		120–125	248–257	152–161	306–322
Brown No. 2		130	266	153	307
Brown No. 3	1.544	117	243	160	320
Brown chips		125	257	162	324
Brown dust		135	275	225	437
Bush bold		90	194	121	250
Bush chips		93	199	127	261

(*Continued*)

Specific Gravity	Direct Acid Number	Indirect Acid Number	Saponification Number	Iodine Number	Solubility Type	Insolubility Type
1.06	107	138	140	125	Alcohols and ketones	Aryl and aliphatic hydrocarbons
1.07	109	130	136	123		
1.07	111	135	143	124		
1.07	114	143	154	120		
1.08	113	135	143	116		
1.07	110	139	148	113		
1.08	110	142	157	104		
1.07–1.08	113–118	122–131	149–180	119–142	Alcohols and ketones	Aryl and aliphatic hydrocarbons, esters
1.07	121	135	148	131		
1.08	118	135	151	127		
1.07–1.08	112–118	126–135	151–180	106		
1.07–1.08	119–120	127–139	154–180	125		
1.07	118	147	143	137	Alcohols and ketones	Aryl and aliphatic hydrocarbons, esters and ethers
1.07–1.08	120–123	145–147	159	110–129		
1.07	122–141	147–150	175	110–133		
	20–35	22–35	21–44	118	Aryl hydrocarbons and esters	Aliphatic hydrocarbons, alcohols and ketones
1.04–1.06	50–70	57	62–90	64–142	Alcohols, aryl hydrocarbons	Aliphatic hydrocarbons
1.34		123	65	200	Alcohols	Aryl and aliphatic hydrocarbons
		133		196		
1.05–1.09	117–155	128–155	145–157	112–141	Alcohols	Aryl and aliphatic hydrocarbons
1.04	62	66	70	148	Alcohols and ketones	Aryl and aliphatic hydrocarbons
1.04	62	72	76	149		
1.04	57	63	67	154		
1.04	64	85	88	132		
1.04	67	88	94	120		
1.03–1.04	81	100	101	107		
1.04	75	93	101	112		
	75	103	117	82		
1.04	66	72	77	141		
1.04	62	74	79	133		
1.04	57–68	67–81	79	120–177		
1.04	68	81	84	114		
1.04	74	104	110	104		
1.04	76	127	117	84		
	62	93	117	56		
1.04	76	79	88	146		
1.05	85	119	124	112		

TABLE XIV

Name of Resin	Refractive Index	Softening Point		Melting Point	
		°C.	°F.	°C.	°F.
Congo					
White and ivory congo					
No. 1 Water-white transparent	1.540	87	189	128	262
No. 2 Cloudy white		84	183	135	275
No. 14 Selected fully scraped ivory		75–91	167–196	143–144	289–291
No. 15 Ord. ivory sorts	1.541	74	165	144	291
No. 16 Inferior ivory sorts		79	174	140	284
No. 24 No. 1 Ivory nubs		89	192	138	280
No. 25 No. 2 Natural ivory nubs		87	189	145	293
Straw colored congo					
No. 3 Selected pale straw bold		89	192	176	349
No. 4 Pale bold straw		81	178	178	352
No. 5 Pale bold straw		85–97	185–207	179–220	354–428
No. 7 Pale straw bold washed		87	189	172	342
No. 18 Pale straw nubs		85	185	161	322
No. 19 Pale straw nubs		89	192	162	324
Pale congo					
No. 17 No. 1 Pale fingers		84	183	174	345
No. 26 Bold pale chips		90	194	144	291
No. 27 Small pale chips		89	192	144	291
No. 28 Pale dust		92	198	147	297
Amber congo					
No. 6 Pale amber bold		101	214	206	403
No. 8 Light amber bold		99	210	169	336
No. 9 Medium light amber bold		94	201	161	322
No. 10 Rescraped hard dark amber		82	180	204	399
No. 11 Hard dark amber bold		91–104	196–219	193–200	379–392
No. 20 Dark hard amber nubs		95	203	162	324
Sorts and selections of congo					
No. 12 Selected sorts bold		86	187	174	345
No. 13 Dark sorts bold		88	190	160	320
No. 21 Selected nubs ordinary		93	199	161	322
No. 22 Small mixed nubs		95	203	143	289
No. 23 Dark mixed nubs		90	194	147	297

*Where single values are given, they are median. Individual lots may show a plus or minus

range of solubility for that resin in that solvent) which supplies the following data:

1. Pounds of resin used per gallon of solvent.
2. Yield in gallons of clear filtered solution.
3. Density in pounds per gallon.
4. Specific gravity.
5. Per cent resin in final solution.

The bulking value of a resin is defined as the volume in gallons

(*Continued*)

Specific Gravity	Direct Acid Number	Indirect Acid Number	Saponification Number	Iodine Number	Solubility Type	Insolubility Type
1.05–1.07	100	115	124	115		
1.06	112	115	124	117		
1.06–1.07	92–94	111–120	119	113	None	All solvents
1.05–1.06	106	118	121	114		
1.06	103	123	127	111		
1.06	95	125	119	116		
1.06	105	127	124	116		
1.06	96	114	124	127		
1.05	100	118	126	133		
1.06–1.07	95–110	119–132	123	131		
1.06	98	119	126	123	None	All solvents
1.05	98	121	129	125		
1.05	106	123	124	132		
1.06	97	122	120	116		
1.06	110	127	132	122	None	All solvents
1.06	115	127	133	118		
	112	128	150	110		
1.05	96	118	124	137		
1.06	95	120	125	124		
1.06	94	120	124	120	None	All solvents
1.06	94	120	126	124		
1.06–1.07	95–102	120–123	123–132	123		
1.06	99	123	124	123		
1.06	101	120	124	128		
1.05	101	119	133	123		
1.06	99	124	127	124	None	All solvents
1.06	109	124	128	121		
1.05	103	124	131	121		

variation.

occupied by one pound of resin when in solution (disregarding the original volume occupied by the solvent and the volume occupied by the insolubles). Since the bulking value thus obtained is an additive function, the previously mentioned values may then be calculated and plotted for the entire range of solubility.

Thus, for manila DBB, a grade widely used in alcohol spirit varnishes, the bulking value dirt-free is 0.087 gal. per lb. The range of insoluble content for manila DBB is from 2.5 to 3.5 per cent. Since the variations are in a narrow range, the intermediate value of 3 per cent

provides a sufficiently accurate basis for calculations. From these two values, together with the specific gravity of the solvent, the data necessary can be readily calculated. (Fig. 20.)

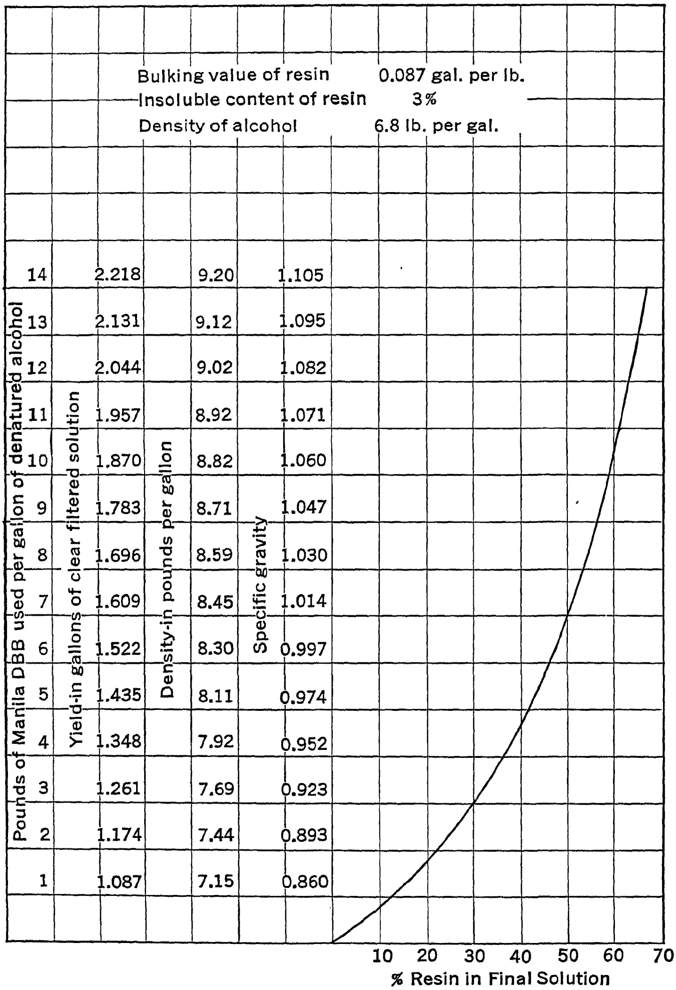


FIG. 20. Yield chart for cold-cutting manila DBB.

In a similar manner, a chart for a resin in any other solvent may be prepared from the bulking value determined for the resin in that particular solvent.

In Table XV are given the bulking values obtained for a variety of

the natural resins in benzol or alcohol. The procedure used in determining the bulking value was to dissolve 0.0924 lb. of resin in 50 cc. of solvent (the equivalent of 7 lb. of resin in 1 gal. of solvent) in a graduated cylinder. The resulting solution was then permitted to stand 24 hours. At the end of this period the increase in volume, due to the resin addition, and the insoluble deposition were recorded (columns A and D). From this increase in volume, the cubic centimeter increase in volume per pound of resin (column B) and the gallons bulked per pound of resin including dirt (column C) can be calculated. Subtracting the value in column D from the value in column A gives the increase in volume due to the dissolved resin (column E). From this value the cubic centimeter increase in volume per pound of dirt-free resin (column F) and the bulking value of the dirt-free resin (column G) are calculated. For congo it is necessary to calculate the bulking value from the specific gravity owing to the peculiar solubility characteristics of the resin. This method is not recommended for soluble resins, however, as it introduces certain unavoidable errors.

Color as Affected by Temperature and Contact with Metals. Natural resins and their solutions darken in color under certain conditions, particularly upon contact with certain metals, notably iron and copper. The reason for this is not known, although it is believed that the latent coloring constituents are of an acidic nature and react with the metals to form complex and colored metallic resinates. The deleterious effect of iron on color is so marked that its use for varnish kettles, storage tanks, and resin-processing equipment, where contact with the metal occurs other than in solid form, is always avoided except where black or dark-colored enamels are to be prepared. Copper has a definite effect upon color, as do copper alloys such as brass and bronze, but much less so than iron. Stainless steel, Monel metal, nickel, and aluminum do not cause discoloration. Lead also shows no effect upon color so that terne-plate containers may be satisfactorily used for storage and shipping purposes.

The natural resins show discoloration or darkening at elevated temperatures, and whether in solid or solution form, will gradually darken when heated. The effect is due in part to oxidation, because run or esterified resins made in an inert atmosphere yield lighter products than when the resin is exposed to air. The depth of color developed is a function of time and temperature. At temperatures in excess of 80°C. the darkening proceeds more rapidly. Natural resin films when baked do not possess an objectionable color (probably owing to the thinness of the film) and bleach rapidly upon exposure to sunlight.

TABLE XV

Column Letter		A	B	C	D	E	F	G	H
Resin	Solvent	Increase in volume, cc. per 0.0924 lb. resin	Increase in volume, cc. per 1 lb. resin	Gal. bulked per 1 lb. resin plus dirt	Cc. deposition per 0.0924 lb. resin	Increase in volume, cc. per 0.0924 lb. resin minus dirt	Increase in volume, cc. per 1 lb. resin minus dirt	Gal. bulked per 1 lb. resin minus dirt	Specific gravity
Elemi	B	41	444	0.117	2	39	422	0.111	...
Accroides (coarse)	A	32	346	0.091	15	17	184	0.049	...
Manila MA	A	37	401	0.106	10	27	292	0.077	...
Manila CBB	A	37.5	406	0.107	4	33.5	362	0.096	...
Pontianak chips	A	37	401	0.106	15	22	238	0.062	...
Manila DBB	A	37.5	406	0.107	7	30.5	330	0.087	...
Congo sorts No. 12*	...	...	...	...	...	...	...	0.1142	1.05
Congo medium pale amber No. 9*	...	...	...	...	...	...	...	0.1132	1.06
Congo pale No. 5*	...	...	...	...	...	...	...	0.1128	1.065
Pontianak bold	A	38	412	0.109	0.5	37.5	406	0.107	...
Batavia damar A/E	B	39	422	0.111	5	34	368	0.097	...
Batavia damar seeds	B	39	422	0.111	6	33	357	0.094	...
Singapore damar dust	B	37	401	0.106	10	27	292	0.077	...
Singapore damar No. 1	B	40	433	0.114	1	39	422	0.111	...
Brown kauri No. 2	A	39	422	0.111	3	36	389	0.103	...
Black east india bold scraped	B	39	422	0.111	5	34	368	0.097	...
Batu bold scraped	B	40	433	0.114	1	39	422	0.111	...
Black east india bold unscraped	B	38	412	0.109	5	33	357	0.094	...
Pale east india macassar nubs	B	39	422	0.111	3	36	389	0.103	...
Pale east india macassar bold	B	38.5	417	0.110	1	37.5	406	0.107	...
Pale east india singapore bold	B	38	412	0.109	1	37	401	0.106	...

* Calculated results.
A Denatured ethyl alcohol.
B Benzol.

Reactivity toward Basic Pigments. Occasional references in the literature pertain to livering of enamels and similar pigmented compositions wherein the difficulty has been attributed to natural resins in the formulation. An investigation was undertaken to determine the relative reactivity of the various natural resins with basic pigments and thus to render predictable the suitability of these resins in inks, enamels, pigmented lacquers, and other pigmented resinous products.

Livering is essentially a partial or complete gelatinization of the

vehicle. It is usually manifested by coagulation or flocculation of the pigment accompanied by increase in consistency. When severe, the increase in consistency continues until the entire material has been transformed into a tough rubbery mass. There may or may not be a concomitant gas formation and the occurrence may be quite rapid or may extend over a period of several months.

One theory attributes livering to insoluble soap formation resulting from the reaction between resin acids or drying oil fatty acids and basic pigments. The tendency to liver usually increases with the acid number of the vehicle employed, but numerous exceptions exist in which the acid value presents no criterion of livering tendencies. Certain organic acids retard livering. The explanation for these apparent discrepancies has been that there is present in the formulation some component in which the soaps are partially or completely soluble.

The second theory stresses the chemical and physical properties of finely dispersed pigment systems as more important. General opinion seems to favor the theory of soap formation as the fundamental cause of livering. Acid value, when high, although not of necessity directly proportioned to livering tendencies, may be indicative of such. Other chemical reactions than those of soap formation may be contributing factors.

Livering may be prevented by reduction of the acid value of the vehicle or its constituents and the addition of materials which serve as saponification retarding agents.

In determining the reactivity or livering tendencies of the natural resins, the procedure[1] consists of mixing the paint liquid with zinc oxide, in the proportions of 35 to 65 parts by weight, making alternate additions of pigment and vehicle in such a manner that a fairly stiff paste is produced, then thinning this paste by addition of the balance of the vehicle and stirring thoroughly. The total time for mixing should not exceed thirty minutes. The temperature of the resulting paint is brought to 25°C. ± 0.5°C. and the consistency determined. The paint is then transferred to a friction-top can, filled to within ¼ in. from the top, and stored at normal room temperature. Preliminary indications of reactivity are determined by a second consistency determination made 24 hours later. Final decisions as to reactivity are based upon a third consistency determination taken five days after preparation of the paint.

In the determination of consistency the Gardner mobilometer was

[1] "Proposed Method of Test for Reactivity of Paint Liquids," *A.S.T.M. Bulletin*, October, 1937.

TABLE XVI

REACTIVITY OF NATURAL RESINS TO BASIC PIGMENTS

Varnish*	Freshly Made		24 Hours Later		5 Days Later		Rating
	No wt. on pan	100 g. on pan	No wt. on pan	100 g. on pan	No wt. on pan	100 g. on pan	
25 gallons {20 gal. CWO†, 5 gal. linseed} Congo No. 11	98.0	47.5	113.1	54.5	144.3	68.0	Moderately reactive
25 gallons {20 gal. CWO, 5 gal. linseed} Congo No. 4 refluxed gum	Livered immediately						Reactive
25 gallons {20 gal. CWO, 5 gal. linseed} Commercial congo ester	6.9	3.5	6.9	3.4	7.4	3.5	Non-reactive
10 gallons Congo No. 13	Livered immediately						Reactive
25 gallons {20 gal. soya, 5 gal. CWO} 75% Congo No. 11 25% Pontianak mixed bold	..	200.3	..	508.3	Livered		Reactive
25 gallons {20 gal. CWO, 5 gal. linseed} Congo No. 4 5% glycerin	17.7	8.0	24.6	10.7	24.5	10.7	Non-reactive
Congo No. 11 2.5% glycerin	141.6	68.1	199.0	96.1	346.4	167.6	Reactive
12 gallons {7 gal. linseed, 5 gal. CWO} Congo No. 11	Livered immediately						Reactive
25 gallons {20 gal. CWO, 5 gal. linseed} Commercial run congo	Livered immediately						Reactive
25 gallons {20 gal. CWO, 5 gal. linseed} Congo No. 11 5% glycerin	38.5	16.6	43.9	22.0	49.0	23.8	Slightly reactive
25 gallons {20 gal. CWO, 5 gal. linseed} Congo No. 11 2.5% glycerin	209.7	97.1	280.4	128.4	537.8	272.2	Reactive
25 gallons {20 gal. CWO, 5 gal. linseed} Congo No. 11 2% glycerin, added to run congo, 2.5% glycerin	71.9	36.8	81.5	38.4	201.9	103.1	Reactive
15 gallons CWO Batavia damar	2.2	1.1	2.2	1.1	2.2	1.1	Non-reactive
25 gallons {85% CWO, 15% linseed} Bold pontianak	60.3	34.2	111.3	51.5	Livered		Reactive
25 gallons {85% CWO, 15% linseed} Manila DBB	Livered immediately						Reactive

* The varnish formulations are to be understood as containing the indicated volumes of oil and 100 lb. of the stated resin. Most of the varnishes in this table are therefore 25-gallon length.

† China wood oil.

TABLE XVI (*Continued*)

Varnish	Freshly Made: No wt. on pan	Freshly Made: 100 g. on pan	24 Hours Later: No wt. on pan	24 Hours Later: 100 g. on pan	5 Days Later: No wt. on pan	5 Days Later: 100 g. on pan	Rating
25 gallons {85% CWO, 15% linseed} Boea medium dark	Livered immediately						Reactive
25 gallons {85% CWO, 15% linseed} Brown kauri No. 1	20.6	11.9	46.0	23.0	66.1	33.2	Moderately reactive
25 gallons {85% CWO, 15% linseed} Bold scraped batu	2.2	1.2	3.0	1.7	4.0	2.0	Non-reactive
25 gallons {85% CWO, 15% linseed} Congo No. 11	3.2	1.7		429.9	Livered		Reactive
25 gallons {85% CWO, 15% linseed} Congo No. 12	2.6	1.5	60.8	29.3	112.7	53.4	Moderately reactive
25 gallons {85% CWO, 15% linseed} Bold scraped black east india	2.8	1.4	4.1	1.7	4.6	2.4	Non-reactive
25 gallons superior soybean oil Batavia damar A	1.3	1.0	1.3	1.0	1.2	0.9	Non-reactive
25 gallons diamond K soybean oil Batavia damar A	2.1	1.2	2.1	1.2	2.1	1.2	Non-reactive
40 gallons superior soybean oil Batavia damar A	1.0	0.8	1.2	1.0	1.2	1.0	Non-reactive
40 gallons diamond K soybean oil Batavia damar A	1.5	1.0	1.8	1.1	2.2	1.2	Non-reactive
40 gallons KPO "B" linseed oil Batavia damar A	1.2	0.9	1.3	1.0	1.5	1.0	Non-reactive
55 gallons superior soybean oil Batavia damar A	1.3	1.0	1.2	0.9	1.2	0.9	Non-reactive
55 gallons KPO "B" linseed oil Batavia damar A	1.3	0.9	1.3	1.0	1.5	1.0	Non-reactive

employed. All values reported are in seconds and are values obtained by averaging a series of determinations made with the four-hole mobilometer disk.

On the basis of the results obtained, the various vehicles are rated as non-reactive, slightly reactive, moderately reactive, or reactive. In thus rating paint vehicles, although theoretically a non-reactive material should show no increase in consistency, such behavior rarely occurs in actual practice. Even in ideal situations where both pigment and

TABLE XVII

Varnish*	Freshly Made		24 Hours Later		5 Days Later		Rating
	No wt. on pan	100 g. on pan	No wt. on pan	100 g. on pan	No wt. on pan	100 g. on pan	
25 gallons {20 gal. CWO† / 5 gal. linseed} Bold pale manila 10% Pure phenolic resin No. 1	Livered immediately						Reactive
25 gallons {20 gal. CWO / 5 gal. linseed} Congo No. 4 10% Pure phenolic resin No. 1	..	232.9	Livered				Reactive
25 gallons {20 gal. CWO / 5 gal. linseed} 75% Pale manila chips 25% Pure phenolic resin No. 2	8.7	4.2	11.5	5.4	24.0	11.6	Slightly reactive
25 gallons {20 gal. CWO / 5 gal. linseed} Congo No. 4 10% Pure phenolic resin No. 1	247.4	136.8	419.6	208.6	959.6	494.2	Reactive
25 gallons {85% CWO / 15% linseed} 75% Bold pontianak 25% Pure phenolic resin No. 3	3.5	1.4	10.3	5.2	26.8	13.1	Slightly reactive
25 gallons {85% CWO / 15% linseed} 50% Bold pontianak 50% Pure phenolic resin No. 3	2.3	1.5	6.9	3.1	10.7	4.9	Non-reactive
25 gallons {85% CWO / 15% linseed} 75% Manila DBB 25% Pure phenolic resin No. 3	2.1	1.3	44.7	22.0	57.3	28.4	Moderately reactive
25 gallons {85% CWO / 15% linseed} 50% Manila DBB 50% Pure phenolic resin No. 3	2.8	1.4	20.8	10.2	22.9	10.9	Slightly reactive
25 gallons {85% CWO / 15% linseed} 75% Boea medium dark 25% Pure phenolic resin No. 3	1.5	1.1	8.1	3.8	13.2	5.8	Slightly reactive
25 gallons {85% CWO / 15% linseed} 50% Boea medium dark 50% Pure phenolic resin No. 3	1.6	1.1	4.3	2.1	4.3	2.1	Non-reactive
25 gallons {85% CWO / 15% linseed} 75% Brown kauri No. 1 25% Pure phenolic resin No. 3	2.0	1.3	9.6	4.7	12.4	5.8	Slightly reactive
25 gallons {85% CWO / 15% linseed} 50% Brown kauri No. 1 50% Pure phenolic resin No. 3	1.5	1.0	1.6	1.0	1.6	1.0	Non-reactive

* The varnish formulations are to be understood as containing the indicated volumes of oil and 100 lb. of the stated resin. Most of the varnishes in this table are therefore 25-gallon length.

† China wood oil.

TABLE XVII (*Continued*)

Varnish	Freshly Made		24 Hours Later		5 Days Later		Rating
	No wt. on pan	100 g. on pan	No wt. on pan	100 g. on pan	No wt. on pan	100 g. on pan	
25 gallons {85% CWO, 15% linseed} 75% Black east india 25% Pure phenolic resin No. 3	1.9	1.0	4.0	2.0	4.0	2.0	Non-reactive
25 gallons {85% CWO, 15% linseed} 50% Black east india 50% Pure phenolic resin No. 3	1.6	1.0	1.6	1.0	1.6	1.0	Non-reactive
25 gallons {85% CWO, 15% linseed} 75% Batu 25% Pure phenolic resin No. 3	3.0	1.6	7.0	3.5	11.6	5.7	Non-reactive
25 gallons {85% CWO, 15% linseed} 50% Batu 50% Pure phenolic resin No. 3	2.0	1.1	3.2	1.6	4.0	2.0	Non-reactive
25 gallons {85% CWO, 15% linseed} 75% Congo No. 11 25% Pure phenolic resin No. 3	2.2	1.2	34.2	16.3	88.4	39.5	Moderately reactive
25 gallons {85% CWO, 15% linseed} 50% Congo No. 11 50% Pure phenolic resin No. 3	3.4	1.5	36.8	17.8	57.7	26.2	Moderately reactive
25 gallons {85% CWO, 15% linseed} 50% Congo No. 11 50% Modified phenolic	2.0	1.3	11.6	5.8	19.8	9.2	Moderately reactive
25 gallons {85% CWO, 15% linseed} 25% Congo No. 11 75% Modified phenolic	2.0	1.3	8.5	4.2	10.8	4.7	Slightly reactive
25 gallons {85% CWO, 15% linseed} 50% Congo No. 12 50% Modified phenolic	2.5	1.4	9.8	4.8	15.3	7.1	Slightly reactive
25 gallons {85% CWO, 15% linseed} 25% Congo No. 12 75% Modified phenolic	2.7	1.6	4.4	2.2	5.4	2.8	Non-reactive
25 gallons {85% CWO, 15% linseed} 50% Brown kauri No. 1 50% Modified phenolic	1.8	1.2	2.3	1.4	2.5	1.5	Non-reactive
25 gallons {85% CWO, 15% linseed} 25% Brown kauri No. 1 75% Modified phenolic	2.5	1.3	3.6	1.8	4.6	2.3	Non-reactive

TABLE XVII (*Continued*)

Varnish	Freshly Made		24 Hours Later		5 Days Later		Rating
	No wt. on pan	100 g. on pan	No wt. on pan	100 g. on pan	No wt. on pan	100 g. on pan	
25 gallons {85% CWO, 15% linseed}; 50% Black east india; 50% Modified phenolic	2.1	1.3	2.3	1.2	2.6	1.4	Non-reactive
25 gallons {85% CWO, 15% linseed}; 25% Black east india; 75% Modified phenolic	2.4	1.4	3.8	1.9	5.2	2.5	Non-reactive
25 gallons {85% CWO, 15% linseed}; Ester gum	2.1	1.2	2.9	1.5	3.9	1.9	Non-reactive
25 gallons {85% CWO, 15% linseed}; 75% Ester gum; 25% Pure phenolic resin No. 3	1.9	1.0	2.7	1.4	3.7	1.7	Non-reactive
25 gallons {85% CWO, 15% linseed}; 50% Ester gum; 50% Pure phenolic resin No. 3	1.9	1.0	2.0	1.3	2.4	1.2	Non-reactive

vehicle are non-reactive materials, consistency increases occur as a result of thixotropy, pigment reflocculation, and surface phenomena common to dispersed systems. Such changes, however, are not often of great magnitude and usually occur within the 24 hours following preparation of the material. Changes of the type described above have been rated as non-reactive rather than as slightly reactive.

All tests conducted have utilized drying oil varnishes. By using a solution of the resin in a neutral solvent, a more exact measure of the reactivity of the resin might be obtained. Since the majority of pigmented formulations contain a drying oil as well as a resin, and since the drying oils do vary in reactivity toward basic pigments, the information is applicable to the customary range of industrial applications.

Those vehicles and resins listed in the following tables as non-reactive or slightly reactive will be suitable for use in formulations employing reactive pigments. Those vehicles and resins listed as moderately reactive or reactive will not be suitable for use with reactive pigments. Such designation does not, however, preclude their use with pigments of a less reactive nature.

In addition to the ordinary varnishes Table XVI also furnishes several examples of the effect of incorporating a small percentage of

glycerin during the cooking of congo varnishes. A study was also made to determine the effect of adding various percentages of non-reactive synthetic resins. The results of this investigation are given in Table XVII.

In Table XVII the pure phenolic resins are all of the heat-reactive type. A determination with ester gum has also been included for purposes of comparison.

In general, it may be stated that the damars, batu, pale and black east india, and commercial congo ester are non-reactive and suitable for use with any type of pigment. The kauris, congos, and Manila copals can be made suitable for use with reactive pigments by esterification, addition of an esterifying agent during the varnish preparation or by addition of varying proportions of phenolic resins. However, in their original state their use must be confined to formulations containing no pigments of a basic nature.

CHAPTER XIII

SOLUBILITY

Solubility in commercial solvents is exceeded in importance only by the film-forming characteristics of the resins. In every application resin solubility and the viscosity of the resulting solution play important roles. Unfortunately, a large portion of the solubility data available in the earlier natural resin literature is contradictory and in many instances it is of dubious value. This condition can be attributed in part to solubility data reported on forestry and other resin samples possessing no industrial significance, and to changes in resin designations. Thus, the solubility data of Kekulot or Meranti damar, for example, are no longer representative solubility data for any grade of damar currently marketed in the United States, nor do they represent the solubility characteristics of the damars as a whole.

The various classes of natural resins show definite solubility and insolubility types.[1] Thus the damars are of the hydrocarbon solubility type and of the alcohol insolubility type, being soluble in a wide range of aliphatic and aromatic hydrocarbons but relatively insoluble in solvents of the alcohol family. By a study of the solubility types it is possible to obtain a rather broad picture of what may be expected with reference to the solubility of natural resins in the various classes of organic solvents. (Table XVIII.)

Resin solutions show no evidence of saturation point, simply becoming more viscous as the concentration of resin increases, and are probably more in the nature of colloidal sols than of true solutions. These are generally spoken of as solutions, however, and the dissolving power of a solvent for a particular resin is considered to vary inversely with the viscosity of a solution of the resin in it. Using the term in this sense, some solvents dissolve the resin completely, some dissolve only part of it, some simply swell the resin particles, some mix with it to form a more or less elastic gelatinous mass, and some do not affect it at all.

The natural resins are heterogeneous in composition. Each is composed actually of a number of different constituents possessing different

[1] C. L. Mantell and R. W. Allan, *Ind. Eng. Chem.*, 30, 262 (1938).

solubility characteristics. For this reason the volume of solvent used does not determine the amount which will go into solution. For purposes of illustration let us assume a solution based upon equal weights of solvent and resin. If, in such a solution, 75 per cent of the resin dissolve, it should not be expected that the addition of more solvent would result in solubility of the previously undissolved 25 per cent. The residual portion is insoluble in that particular solvent and the addition of further solvent serves only to reduce the viscosity.

The solubility limits of resins in solvents should not be thought of as similar to those of salts in water where definite quantitative limits can be assigned in terms of grams of salt per liter of water at any specified temperature. This is not possible for resin solutions (which are really colloidal systems). The phenomenon of mutual solubility exists in such systems, i.e., the resin dissolves in the solvent but the solvent also dissolves in the resin. The degree to which each preponderates depends upon the relative quantities of resin and solvent used. As long as complete intermixing of a soluble resin and its solvent is possible, the solubility limit is theoretically infinite. Actually, when high resin contents are reached, the formation of a gel prevents further solution.

The many discrepancies and the incompleteness of natural resin solubility data available in the literature have led to an intensive investigation of natural resin solubility characteristics. The investigation was undertaken not with the intention of obtaining data of analytical precision, but rather to supply a comprehensive survey of the solubility of representative natural resins sufficiently accurate to provide criteria as to the suitability of the various natural resins for specific industrial purposes. The solvents were chosen to give ample representation of the commercial solvents of each class and to give, in addition, as wide a selection as possible from among all types of solvents available in commercial quantities.

The study includes some 5,000 solubility determinations which were conducted according to the following procedure: One-hundred-gram samples of each resin, ground to a split-pea size, were placed in 12-oz. cylindrical screw-cap jars, and 100 g. of solvent added. The jars were then rotated on a mixing machine at about 30 r.p.m. for approximately 15 to 18 hours at room temperature. Since the jars were only about two-thirds full and were rotated in the plane of their vertical axes, ample mixing was obtained. After removal from the rotating mechanism, the jars were permitted to stand 24 hours for the contents to settle. They were then examined for the amount and condition of the

TABLE XVIII

Solubility Classification

Type of Resin	Name	Solubility Type	Insolubility Type	Soluble in	Largely Soluble in	Insoluble or Swollen in
Fossil copal	Congo	None	All solvents	......	......	......
	Kauri	Alcohols, ketones	Aryl and aliphatic hydrocarbons	Alcohols (ethyl, butyl, amyl), acetates, ketones, alcohol-ethers, aniline, dioxane, phenol, tetralin	......	Coal-tar hydrocarbons, terpenes, chlorinated compounds, hexalin, nitrobenzene, tricresyl phosphate, petroleum hydrocarbons
Manila copal	Melengket (soft manilas, MA, MB)	Alcohols, esters, ketones	Aryl and aliphatic hydrocarbons	Alcohols, ketones, alcohol-ethers	......	Petroleum hydrocarbons, coal-tar hydrocarbons, chlorinated compounds, terpenes
	Loba (half-hard)	Alcohols, ketones	Aryl and aliphatic hydrocarbons	Alcohols, ketones, low-molecular-weight esters, Cellosolve, Cellosolve acetate	Aniline, phenol, butyl acetate, butyl lactate	Petroleum hydrocarbons, coal-tar hydrocarbons, chlorinated compounds, high-molecular-weight esters, terpenic compounds
	Pontianak (fossil or hard)	Alcohols, ketones	Aryl and aliphatic hydrocarbons, esters	Alcohols, ketones, low-molecular-weight alcohol-ethers, ethyl ether, acetates (ethyl, butyl, amyl)	Butyl Carbitol, Cellosolve acetate, aniline, phenol	Petroleum hydrocarbons, coal-tar hydrocarbons, chlorinated compounds, terpenic compounds
	Boea (fossil or hard)	Alcohols, ketones	Aryl and aliphatic hydrocarbons, esters, ethers	Phenol	Alcohols, ketones	Chlorinated compounds, coal-tar hydrocarbons, esters, ethers, terpenes, alcohol-ethers, aniline, dioxane, hexalin, nitrobenzene, tetralin, petroleum hydrocarbons
Damar	Batavia, Singapore	Aryl and aliphatic hydrocarbons, terpenes	Alcohols, esters	Chlorinated compounds, coal-tar hydrocarbons, petroleum, terpenes, carbon disulfide, tetralin, paraffin, hydrogenated and naphthenic petroleum naphthas	......	Alcohols, alcohol-ethers, alcohol-esters, Cellosolve acetate, acetic acid, aniline, ethylene glycol diethyl ether, ethylene oxide, glycol diacetate, hexalin, nitrobenzene, phenol, propylene oxide, tricresyl phosphate, diethylene oxide
Miscellaneous	Batu, black east india	Aryl and hydrogenated aliphatic hydrocarbons	Alcohols, esters, ethers, ketones, terpenes	Chlorinated compounds, coal-tar hydrocarbons, Cellosolve acetate, hydrogenated petroleum solvents; black east india in some paraffinic type	......	Alcohols, esters, ethers, ketones, terpenes, alcohol-ethers, alcohol-esters, acetic acid, aniline, dioxane, glycol diacetate, hexalin, nitrobenzene, phenol, tetralin, naphthenic petroleum hydrocarbons
	Pale east india	Aryl and hydrogenated aliphatic hydrocarbons	Alcohols, esters, ketones	Hydrogenated and some paraffinic petroleum hydrocarbons, chlorinated compounds, coal-tar hydrocarbons	Ethers, terpenes, linoleic acid, tetralin	Alcohols, esters, ketones, alcohol-ethers, acetic acid, aniline, dioxane, hexalin, nitrobenzene, phenol, tricresyl phosphate
	Accroides (red gum)	Alcohols	Aryl and aliphatic hydrocarbons	Alcohols, esters, ketones	Cellosolve acetate, Cellosolve, acetic acid, aniline, dioxane, phenol	Chlorinated compounds, coal-tar hydrocarbons, petroleum hydrocarbons, ethers, terpenes, carbon tetrachloride, hexalin, tetralin, nitrobenzene, tricresyl phosphate, alkali solutions
	Elemi	Aryl hydrocarbons, esters	Aliphatic hydrocarbons, alcohols, ketones	Coal-tar hydrocarbons, esters	Alcohol-ethers, glycol monoacetate, carbon disulfide, dioxane, ethylene glycol diethyl ether, ethylene oxide, glycol diacetate, hexalin, phenol, propylene oxide, tetralin	Chlorinated compounds, ketones, Cellosolve acetate, acetic acid, aniline, glycol ether acetate, nitrobenzene, tricresyl phosphate, petroleum hydrocarbons
	Mastic	Alcohols, aryl hydrocarbons	Aliphatic hydrocarbons	Alcohols, coal-tar hydrocarbons, esters, ethers, alcohol-ethers	Cellosolve acetate, aniline, dioxane, ethylene glycol diethyl ether, ethylene oxide, glycol diacetate, glycol ether acetate, nitrobenzene, phenol, propylene oxide, tetralin, methyl acetone	Acetone, alcohol-esters, acetic acid, carbon disulfide, hexalin, paraffinic and naphthenic petroleum solvents
	Sandarac	Alcohols	Aryl and aliphatic hydrocarbons	Alcohols, ketones, alcohol-ethers, Cellosolve acetate, aniline, dioxane, ethylene oxide, propylene oxide		Chlorinated compounds, coal-tar hydrocarbons, esters, ethers, terpenes, alcohol-esters, acetic acid, carbon disulfide, ethylene glycol diethyl ether, glycol diacetate, glycol ether acetate, hexalin, nitrobenzene, phenol, propylene oxide, tetralin, petroleum hydrocarbons

undissolved resin and the character of the solution or gelatinous phase, if such were formed.

In describing the effect of the solvent upon the resin, the following terms are used:

I Insoluble; resin unaffected by solvent.

SW Swelled; the resin does not necessarily lose its shape. A layer of more or less pure solvent may be above the resin.

NF Non-flowing gel; a non-flowing gelatinous mass has formed on standing.

TVG Transparent viscous gel; the resin and solvent have entirely combined to form a viscous mass, and the original shape of the pieces has been lost.

GL Gelatinous liquid. (More fluid than TVG.)

SLS Slightly soluble; 5 to 25 per cent of the resin has been dissolved by the solvent.

PS Partly soluble; 25 to 50 per cent of the resin has been dissolved.

LS Largely soluble; 50 to 90 per cent of the resin has been dissolved.

S Soluble; all the resin, except for any foreign material, has gone into solution.

The percentages listed are approximate. They were determined by observation, making due allowance for any swelling action of the solvent. Where closer approximations were thought desirable, the undissolved material was removed from the solution, washed once with solvent, dried, and then weighed.

The tables in this book emphasize the importance of the solvent, first in its solution of the resin, and secondly in the effect on the viscosity of the resulting solution. It is not generally appreciated that different petroleum solvents may give relatively wide ranges of viscosity with the same resin and the same concentration of resin, or that variations in the character of the petroleum solvent may make a difference between solubility and partial or slight solubility.

In the description of the results of solubility tests, the terms "slightly soluble," "partly soluble," and "largely soluble" may show cases where the solvent separates the complex resin into soluble and insoluble parts. The term "gelatinous liquid" and "transparent viscous gel" may indicate that most of the resin is in solution and only a small percentage of colloidal insoluble material is left which gels the resulting solution. When solubility is recorded by the designation "soluble" in the chart, the solvent, used alone, will be satisfactory for solution of the resin. Those materials which show lesser solvency, however, may be

very valuable as modifying or cheapening agents for use with stronger solvents. In this case the several designations "largely soluble," "partly soluble," "slightly soluble" can be employed as indicating the identity and quantity of such solvent which may be used. In the use of the term "insoluble," an indication may be obtained as to what solvents a film of the resin may be expected to resist. This will hold true for spirit- or solvent-type varnishes or coatings.

In the majority of those cases in which a resin shows solubility or partial solubility in one of the more important commercial solvents, the color and viscosity of the resulting solutions have also been determined. Color is reported in terms of Gardner color standards and viscosity in terms of the Gardner-Holdt bubble viscosimeter. Viscosities have also been reported in absolute units in order to facilitate direct comparison with results obtained by other methods.

Such a wide variety of petroleum naphthas are available on the present market that it was thought advisable to incorporate the results obtained in a table separate from those of the other organic solvents.

Congo is in a class by itself because of its total insolubility. Kauri and the Manila copals, including the soft manilas, loba, pontianak, and boea, generally show solubility in the alcohols and insolubility in the hydrocarbons, whether of the coal-tar or petroleum type. In contrast, the damars, in which class Batavia, Singapore, batu, and the black and pale east indias fall, show solubility in petroleum as well as coal-tar solvents, and insolubility in the alcohols. A fourth group of resins of the spirit-varnish type includes accroides, mastic, and sandarac, which show, in general, alcohol solubility and insolubility in the aliphatic and petroleum hydrocarbons. Mastic is somewhat of an exception in this group because it shows solubility in aryl or coal-tar hydrocarbons. Elemi is in a class by itself; it is soluble in coal-tar hydrocarbons and insoluble in petroleum hydrocarbons. The individual resins are tabulated separately to indicate their ready solubility, their marked but not complete solubility, and their insolubility.

Accroides. Accroides or red gum is, in general, largely soluble in alcohols of either the anhydrous or denatured type, esters, ketones, ethyl ether, and Cellosolve. It is also largely soluble in dioxane, aniline, phenol at 60°C., glacial acetic acid, and Cellosolve acetate. It is insoluble, or, at most, only partly soluble in chlorinated compounds, coal-tar solvents, ethers higher than ethyl in molecular weight, terpenes other than terpineol, Carbitol, butyl Carbitol, hexalin, tetralin, nitrobenzene, tricresyl phosphate, phenol at 25°C., carbon disulfide,

TABLE XIX. Solubility, Viscosity and Color

		Accroides				Batavia Damar							
						A/D				A/E			
		Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color
1	Acetic acid	GL				PS				PS			
2	Acetone	GL				PS	A−	−0.50	4	PS	A−	−0.50	4
3	Acetylene tetrachloride	PS				S	W	10.70	5	S	V	8.84	5
4	Amyl acetate	LS				S	A−	−0.50	4	S	A−	−0.50	4
5	Amyl acetate, secondary	S	F	1.40	18+	S	A−	−0.50	3	S	A−	−0.50	4
6	Amyl alcohol, normal	S	J	2.50	18+	PS				PS			
7	Amyl alcohol, secondary	S	G	1.65	18+	LS	A	0.50	3	LS	C	0.85	2
8	Amyl alcohol, tertiary	S	X	12.9	18+	PS				PS			
9	Amyl chloride	I				S	A−	−0.50	7	S	A−	−0.50	9
10	Aniline	LS				SW				SW			
11	Ansol	S	A−	−0.50	18+	PS	A−	−0.50	3	PS	A−	−0.50	3
12	Benzol	I				S	A	0.50	4	S	A−	−0.50	4
13	Benzyl alcohol	S	U	6.27	18+	LS				LS			
14	Butyl acetate	LS				LS	A−	−0.50	3	LS	A−	−0.50	2
15	Butyl acetate, secondary	S	D	1.00	18+	LS	A−	−0.50	5	LS	A−	−0.50	6
16	Butyl alcohol, normal	S	C	0.85	18+	PS	A	0.50	4	PS	A−	−0.50	4
17	Butyl alcohol, secondary	S	E	1.25	18+	PS				PS			
18	Butyl alcohol, tertiary	S	V	8.84	18+	PS				PS			
19	Butyl butyrate	S	E	1.25	18+	S				S			
20	Butyl Carbitol	PS				LS	C	0.85	5	LS	C	0.85	4
21	Butyl Cellosolve	LS				PS				PS			
22	Butyl ether	I				S	A−	−0.50	2	S	A−	−0.50	2
23	Butyl lactate	LS				LS	B	0.65	5	LS	C	0.85	3
24	Butyl propionate	S	C	0.85	18+	S				S			
25	Carbitol	PS				PS				PS			
26	Carbitol acetate	PS				PS				PS			
27	Carbon disulfide	SW				S				S	A−	−0.50	5
28	Carbon tetrachloride	I				S	Y	17.6	5	S	W	10.70	5
29	Cellosolve	LS				PS	A	0.50	6	PS	A	0.50	4
30	Cellosolve acetate	S	E	1.25	18+	PS				PS			
31	Chlorbenzol	I				S	A−	−0.50	4	S	A−	−0.50	3
32	Chloroform	NF				S				S			
33	Coal tar naphtha	SLS				S				S			
34	Denatured alcohol No. 1	S	A−	−0.50	18+	PS				PS			
35	Denatured alcohol No. 5	S	A−	−0.50	18+	PS				PS			
36	Diacetone alcohol	PS				PS	A−	−0.50	5	PS	A−	−0.50	5
37	Dibutyl phthalate	PS				LS				LS			
38	Dichloroethyl ether	PS				LS	A−	−0.50	4	LS	A	0.50	5
39	Diethyl carbonate	LS				LS	A−	−0.50	4	LS	A−	−0.50	3
40	Diethylene glycol	S				I				I			
41	Diethylene glycol butyl ether	PS				LS				LS			
42	Diethylene glycol ethyl ether	PS				PS				PS			
43	Diethylene glycol ethyl ether acetate	PS				PS				PS			
44	Diethylene glycol methyl ether	PS				PS				PS			
45	Diethylene glycol monoacetate												

* All determinations made with

S Soluble, 90–100% of resin dissolved.
LS Largely soluble, 50–90% of resin dissolved.
PS Partly soluble, 25–50% of resin dissolved.
SLS Slightly soluble, 5–25% of resin dissolved.
NF Non-flowing gel.

of Natural Resins and Their Solutions*

Batavia Damar "E" seeds				Batavia Damar Dust				Batu East India Nubs and Chips				Black East India Bold Scraped				Boea Hard Bold Amber				
Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	
PS				PS				I				I				S	Y	17.6	4	1
PS				PS				I				I				LS	J	2.50	2	2
S	V	8.84	5	S				SW				SW				SW				3
S				S				SW				I				GL				4
S				S	A−	−0.50	7	NF				GL				PS				5
PS				PS				SW				SW				S	Z	22.7	6	6
LS				LS				I				SW				LS	X	12.9	3	7
PS				PS				PS				SLS				LS				8
S				S				SW				S	Y	17.6	18+	GL				9
SW				SW				SW				I				GL				10
PS				PS				I				I				S	R	4.70	6	11
S				S				S	Z2	36.2	18	S	W	10.70	15	GL				12
LS				LS				SW				SW				GL				13
LS				LS				SW				SW				GL				14
LS	A−	−0.50	8	LS				PS				SLS				PS				15
PS				PS				I				I				S	Z	22.7	6	16
PS	E	1.25	9	PS				PS				SLS				S	Q	4.35	4	17
PS				PS				PS				SLS				LS				18
S				S				NF				NF				S	W	10.70	2	19
LS				LS				SW				I				GL				20
PS				PS				SW				I				S				21
S				S				S	U	6.27	13	S	V	8.84	13	GL				22
LS				LS				SW				I				GL				23
S				S				PS				PS				GL				24
PS				PS				GL				I				GL				25
PS				PS				GL				I				S				26
S	A−	−0.50	8	S	B	0.65	12	S	V	8.84	18+	S	V	8.84	18+	GL	V	8.84	18+	27
S				S				SW				SW				SW				28
PS				PS				SW				I				LS	X	12.9	6	29
PS				PS				S	H	2.00	18+	SLS				S	Y-Z	17.6–22.7	4	30
S				S				LS	Z6	148.0	18	S	Y	17.6	15	GL				31
S				S				GL				S	Z	22.7	15	S			7	32
S				S				S				S				GL				33
PS				PS				PS				PS				S	N	3.40	1	34
PS				PS				PS				PS				S	G	1.65	12	35
PS				PS				I				SLS				S	Z2	36.2	5	36
LS				LS				SLS				SLS				TVG				37
LS				LS				SW				I				SW				38
LS				LS				I				I				GL				39
I				I				SLS				SLS				SLS				40
LS				LS				SW				I				GL				41
PS				PS				GL				I				GL				42
PS				PS				GL				I				S				43
PS				PS				SLS				I				S				44
																				45

100 g. of resin and 100 g. of solvent.

I Insoluble, resin unaffected by solvent.
SW Swelled, resin so affected by solvent.
TVG Transparent viscous gel formed.
GL Gelatinous liquid resulted.

TABLE XIX

		Congo															
		No. 1 Water-white				No. 4 Pale Bold Straw				No. 11 H.D. Amber Bold				No. 21 Selected Nubs			
		Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color
1	Acetic acid	I				I				I				I			
2	Acetone	GL				SW				SW				SW			
3	Acetylene tetrachloride	I				I				I				I			
4	Amyl acetate	GL				TVG				SW				TVG			
5	Amyl acetate, secondary	GL				GL				GL				GL			
6	Amyl alcohol, normal	I				I				I				I			
7	Amyl alcohol, secondary	GL				TVG				SW				TVG			
8	Amyl alcohol, tertiary	GL				GL				GL				GL			
9	Amyl chloride	I				SW				SW				SW			
10	Aniline	GL				SW				SW				TVG			
11	Ansol	GL				TVG				SW				TVG			
12	Benzol	SW				I				SW				SW			
13	Benzyl alcohol	GL				SW				SW				SW			
14	Butyl acetate	GL				TVG				SW				TVG			
15	Butyl acetate, secondary	GL				GL				GL				GL			
16	Butyl alcohol, normal	GL				TVG				SW				TVG			
17	Butyl alcohol, secondary	GL				GL				NF				GL			
18	Butyl alcohol, tertiary	GL				GL				GL				GL			
19	Butyl butyrate	I				I				I				I			
20	Butyl Carbitol	GL				SW				SW				SW			
21	Butyl Cellosolve	SLS				SLS				SLS				SLS			
22	Butyl ether	I				I				I				I			
23	Butyl lactate	GL				SW				SW				SW			
24	Butyl propionate	I				I				I				I			
25	Carbitol	I				I				TVG				I			
26	Carbitol acetate	I				I				TVG				I			
27	Carbon disulfide	TVG				TVG				SW				GL			
28	Carbon tetrachloride	SW				SW				SW				SW			
29	Cellosolve	GL				TVG				SW				SW			
30	Cellosolve acetate	GL				GL				GL				GL			
31	Chlorbenzol	GL				SW				SW				SW			
32	Chloroform	TVG				TVG				NF				NF			
33	Coal tar naphtha	I				SW				SW				SW			
34	Denatured alcohol No. 1	I				I				I				I			
35	Denatured alcohol No. 5	I				I				I				I			
36	Diacetone alcohol	GL				TVG				SW				TVG			
37	Dibutyl phthalate	SLS				SLS				SLS				SLS			
38	Dichloroethyl ether	I				TVG				SW				TVG			
39	Diethyl carbonate	I				TVG				SW				SW			
40	Diethylene glycol	I				TVG				I				I			
41	Diethylene glycol butyl ether	I				TVG				I				I			
42	Diethylene glycol ethyl ether	I				TVG				I				I			
43	Diethylene glycol ethyl ether acetate	I				TVG				I				I			
44	Diethylene glycol methyl ether	GL				GL				GL				GL			
45	Diethylene glycol monoacetate	I				TVG				I				I			

* All determinations made with

Soluble, 90–100% of resin dissolved.
LS Largely soluble, 50–90% of resin dissolved.
PS Partly soluble, 25–50% of resin dissolved.
SLS Slightly soluble, 5–25% of resin dissolved.
NF Non-flowing gel.

*(Continued)**

Congo Ester				East India Macassar								East India Singapore								
				Bold				Nubs				Bold				Nubs				
Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	
I				I				I				I				I				1
SW				I				I				I				I				2
S	Z3	46.3	18+	SW				SW				SW				SW				3
S	E	1.25	18	LS				LS				LS				LS				4
S	E	1.25	18	LS				LS				LS				LS				5
S	V	8.84	18+	SLS				SLS				SLS				SLS				6
S	R	4.70	18+	I				I				I				I				7
S	V	8.84	18+	SLS				SLS				SLS				SLS				8
S	H	2.00	18+	S				S	N	3.40	18+	LS				LS	E	1.25	15	9
S	Z	22.7	18+	SW				SW				SW				SW				10
I				I				I				I				I				11
S	B	0.65	18	S				S	L	3.00	13	S				S	P	4.00	13	12
LS	Z	22.7	18+	I				I				I				I				13
S	C	0.85	18	PS				PS				PS				PS				14
S	F	1.40	18+	PS				PS				PS				PS				15
SW				I				I				I				I				16
SW				PS				PS				PS				PS				17
SW				SLS				SLS				SLS				SLS				18
S	G	1.65	18	LS				LS				GL				GL				19
PS				SLS				SLS				SLS				SLS				20
S	U	6.27	18+	SLS				I				SLS				I				21
S	C	0.85	18	S				S	E	1.25	8	S				S	G	1.65	10	22
LS	V	8.84	18+	I				SW				I				SW				23
S	D	1.00	18	SW				SW				SW				SW				24
SW				I				I				I				I				25
PS				I				I				I				I				26
S	F	1.40	18+	S				S	H	2.00	18	S				S	I	2.25	16	27
SW				SLS				SLS				SLS				SLS				28
SLS				I				I				I				I				29
SLS				I				I				I				I				30
S	G	1.65	18+	S				S	Q	4.35	13	S				S	T	5.50	15	31
S	O	3.70	18+	S				S	X	12.9	18+	S				S	Y-Z	17.6–22.7	13	32
S	E	1.25	18	S				S				S				S				33
I				I				I				I				I				34
I				I				I				I				I				35
SLS				I				I				I				I				36
PS				SLS				SLS				SLS				SLS				37
S	W	10.70	18+	I				SW				I				SW				38
S	K	2.75	18	I				I				I				I				39
SLS				SLS				SLS				SLS				SLS				40
S				I				SW				I				SW				41
SW				I				I				I				I				42
PS				I				I				I				I				43
SW				I				I				I				I				44
																				45

100 g. of resin and 100 g. of solvent.

I Insoluble, resin unaffected by solvent.
SW Swelled, resin so affected by solvent.
TVG Transparent viscous gel formed.
GL Gelatinous liquid resulted.

TABLE XI[illegible]

		Elemi				Kauri								Manila		
						Pale No. 2				Brown No. 2				WS		
		Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises
1	Acetic acid	PS				S	Y	17.6	15	GL				PS		
2	Acetone	PS				S	N	3.40	12	S	P	4.00	18	S		
3	Acetylene tetrachloride	PS				NF				NF				NF		
4	Amyl acetate	S				S	X	12.9	12	S	X	12.9	18	S		
5	Amyl acetate, secondary	S	A–	–0.50	5	S	Y	17.6	13	S				S	W	10.70
6	Amyl alcohol, normal	SLS				S	X–Y	12.9–17.6	13	S	Z2–Z3	36.2–46.3	18+	S	V	8.84
7	Amyl alcohol, secondary	LS	A–	–0.50	1	S	X	12.9	12	S	X	12.9	18	S	Z1	27.0
8	Amyl alcohol, tertiary	S	A	0.50	5	LS	Z	22.7	14	LS				S	Z–Z1	22.7–27.0
9	Amyl chloride	PS				I				I				SLS		
10	Aniline	GL				S	Z4	63.4	18+	LS				S	Z3	46.3
11	Ansol	PS	A–	–0.50	2	S	Q	4.35	12	S	R	4.70	18	S	G	1.65
12	Benzol	S				I				SW				GL		
13	Benzyl alcohol	LS	A	0.50	1	S	Z4	63.4	12–13	S	Z3	46.3	18+	S	Z2	36.4
14	Butyl acetate	S				S	W	10.70	11	S	X	12.9	18	S	Q	4.35
15	Butyl acetate, secondary	S	A–	–.50	5	S	W	10.70	13	S				S	U	6.27
16	Butyl alcohol, normal	S				S	W	10.70	12	S	W	10.70	18	S	R	4.70
17	Butyl alcohol, secondary	LS				S	X	12.9	13	S	Y	17.6	17	S	U	6.27
18	Butyl alcohol, tertiary	PS				PS				PS				S	Y	17.6
19	Butyl butyrate	S				S	Y	17.6	12	S	Z1	27.0	15	S	Y	17.6
20	Butyl Carbitol	PS				S	Z4	63.4	12	S	Z4	63.4	18+	LS	U	6.27
21	Butyl Cellosolve	S				S	W	10.70	14	S	Z2	36.2	18+	LS	K–L	2.75–3.00
22	Butyl ether	PS				I				SW				SW		
23	Butyl lactate	PS				S	Z3–Z4	46.3–63.4	11	S	Z4–Z5	63.4–98.5	18+	LS		
24	Butyl propionate	S				S	X	12.9	13	S	Z–Z1	22.7–27.0	18+	S	W	10.70
25	Carbitol	SLS				I				I				LS		
26	Carbitol acetate	SLS				I				I				I		
27	Carbon disulfide	S	A–	–0.50	4	NF				NF				GL		
28	Carbon tetrachloride	PS				SW				SW				NF		
29	Cellosolve	PS				S	Z	22.7	12	S	X	12.9	18	S	O	3.70
30	Cellosolve acetate	PS				S	Y	17.6	12	S	Z–Z1	22.7–27.0	17	S	V–W	8.84–10.70
31	Chlorbenzol	LS	A–	–0.50	1	S	Z6+	148.0+	12	S	Z6+	148.0+	18+	GL		
32	Chloroform	S				TVG				GL				TVG		
33	Coal tar naphtha	LS				I				SW				I		
34	Denatured alcohol No. 1	PS				S	P	4.00	14	S	X–Y	12.9–17.6	18+	S		
35	Denatured alcohol No. 5	PS												S		
36	Diacetone alcohol	SLS				S	Z	22.7	13	S	Z2	36.2	18	S	Y	17.6
37	Dibutyl phthalate	GL				SLS				SLS				SW		
38	Dichloroethyl ether	SLS				SW				SW				SW		
39	Diethyl carbonate	PS				SW				SW				SW		
40	Diethylene glycol	I				SLS				SW				SLS		
41	Diethylene glycol butyl ether	PS				S	Z4	63.4	12	S	Z4	63.4	18+	LS	U	6.27
42	Diethylene glycol ethyl ether	SLS				I				I				LS		
43	Diethylene glycol ethyl ether acetate	SLS				I				I				I		
44	Diethylene glycol methyl ether	SLS				S	Z4–Z5	63.4–98.5	13	S	Z5	98.5	18+	S	X	12.9
45	Diethylene glycol monoacetate	SLS												I		

* All determinations made w

S Soluble, 90–100% of resin dissolved.
LS Largely soluble, 50–90% of resin dissolved.
PS Partly soluble, 25–50% of resin dissolved.
SLS Slightly soluble, 5–25% of resin dissolved.
NF Non-flowing gel.

(*Continued*)*

Manila				Manila Loba																
MA				B				C				D				DK				
Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	
PS				PS				PS				PS				PS				1
S				S				S	B	0.65	5	S				S				2
NF				NF				SW				NF				NF				3
S				S				S	T	5 50	6	S				S	O	3.70	9–10	4
S	V	8.84	11	S	U	6.27	5	S	V	8.84	6	S	W	10.70	7	LS	V	8 84	11	5
S	U	6.27	12	S	V	8.84	5	S	X	12.9	6	S	W	10.70	11	S	S	5.00	12	6
S	U	6.27	10	S	Q	4.35	6	S	V	8.84	6	S	V	8.84	7	LS	N	3 40	12	7
S	Y	17.6	10	S	X	12.9	6	S	Z3	46.3	7	S	Z1–Z2	27.0–36.2	7	LS	Y	17.6	12	8
SLS				SLS				SLS				SLS				SLS				9
S	X–Y	12.9–17.6	18+	S	Z1–Z2	27.0–36.2	18+	S	Z3	46.3	17	S	Z1	27.0	18+	S	Z1	27.0	18+	10
S	E	1.25	10	S	H	2.00	5	S	J	2.50	7	S	E	1.25	9	S	A	0.50	12	11
GL				GL				GL				GL				GL				12
LS	Z1–Z2	27.0–36.4	11	GL				GL				GL				GL				13
S	N	3.40	10	S	T	5.50	5	S	T	5.50	6	S	V	8 84	7	S	J	2 50	10	14
S	P	4.00	10	S	L	3.00	6	S	X	12.9	6	S	V	8 84	7	S	L	3.00	9	15
S	N	3.40	12	S	V	8.84	5	S	V	8.84	6	S	W	10.70	11	S	I	2.25	12	16
S	S	5.00	8	S	V	8.84	5	S	X	12.9	6	S	U	6 27	7	S	P	4 00	9	17
S	Y	17.6	8	S	Z1	27.0	5	S	Z	22.7	5	S	Z1	27.0	7	S	X	12 9	11	18
S	W	10.70	10	S	W	10.70	4	S	W	10.70	5	S	Y–Z	17.6–22.7	7	S	V	8.84	12	19
LS	U–V	6.27–8.84	11	LS	W	10.70	5	LS	Y	17.6	5	LS	Y–Z	17 6–22.7	7	LS	X–Y	12 9–17.6	12	20
LS	K–L	2.75–3.00	9	S	S	5.00	6	S	X	12.9	5	S	X	12.9	7	S	U	6.27	9	21
SW				SW				SW				SW				SW				22
LS	X	12.9	12	LS	W	10.70	6	LS	Y	17.6	5	LS	Z1	27.0	7	LS	X–Y	12 9–17.6	12	23
S	U–V	6.27–8.84	9–10	LS	R	4.70	5	LS	W	10.70	6	LS	X	12.9	7	LS	Q	4.35	12	24
LS				S				S				S				S				25
I				I				I				I				I				26
GL				GL				GL				GL				GL				27
NF				SW				SW				SW				SW				28
S	O	3.70	12	S	U	6.27	5	S	U	6.27	6	S	R	4.70	11	S	I	2.25	12	29
S	V	8.84	10	S	W	10.70	5	S	V	8.84	6	LS				S	S	5.00	11	30
GL				GL				GL				GL				GL				31
TVG				GL				NF				NF				GL				32
I				I				I				I				I				33
S				S				S				S				S				34
S				S				S				S				S				35
S	Y	17.6	11	S	Z	22.7	5	S	Z	22.7	7	S	Z	22.7	11	S	W	10.70	12	36
SW				SW				SW				SLS				SLS				37
SW				SW				SW				SW				SW				38
SW				SW				SW				SW				SW				39
SLS				SLS				SLS				SLS				SLS				40
LS	U–V	6.27–8.84	11	LS	W	10.70	5	LS	Y	17.6	5	LS	Y–Z	17.6–22.7	7	LS	X–Y	12.9–17.6	12	41
				S				S				S				S				42
I				I				I				I				I				43
S	X–Y	12.9–	12	S	Y–Z	17.6–	5	S	X–Y	12.9–	7	S	X–Y	12.9–	7	S	V	8.84	9	44
		17.6				22.7				17.6				17.6						45

100 g. of resin and 100 g. of solvent.

I	Insoluble, resin unaffected by solvent.
SW	Swelled, resin so affected by solvent.
TVG	Transparent viscous gel formed.
GL	Gelatinous liquid resulted.

TABLE XIX

		Manila Loba (continued)								Manila							
		CNE				Dust				CBB				DBB			
		Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color
1	Acetic acid	PS				PS				PS				PS			
2	Acetone	S				S				S	C	0.85	5	S	A–	–0.50	10
3	Acetylene tetrachloride	NF				SW				SW				SW			
4	Amyl acetate	S	S	5.00	7	S	E	1.25	14	S	T	5.50	6	S	M	3.20	10
5	Amyl acetate, secondary	S	U	6.27	9	LS	J	2.50	12	S	Y-Z	17.6–22.7	7	S	X	12.9	8
6	Amyl alcohol, normal	S	V	8.84	9	S	E	1.25	14	S	X	12.9	7	S	V	8.84	10
7	Amyl alcohol, secondary	S	T	5.50	9	S	D	1.00	14	S	U	6.27	6	S	R	4.70	10
8	Amyl alcohol, tertiary	S				S	T	5.50	18+	S	Z1	27.0	7	S	T	5.50	7
9	Amyl chloride	SLS				SLS				SLS				SLS			
10	Aniline	S	Z	22.7	18+	S	U	6.27	18+	S	Z2–Z3	36.2–46.3	18+	S	Z2	36.2	18+
11	Ansol	S	F	1.40	9	S	A–	–0.50	15	S	H	2.00	8	S	C	0.85	9
12	Benzol	GL				GL				GL				GL			
13	Benzyl alcohol	GL				GL				GL	Z	22.7	9	S	W	10.70	9–10
14	Butyl acetate	S	K	2.75	6	S	E	1.25	13	S	R	4.70	7	S	T	5.50	7
15	Butyl acetate, secondary	S	R	4.70	8	S	B	0.65	14	S	U	6.27	7	S	S	5.00	9
16	Butyl alcohol, normal	S	S	5.00	10	S	C	0.85	14	S	U	6.27	8	S	M	3.20	9
17	Butyl alcohol, secondary	S	P	4.00	9	S	G	1.65	14	S	V	8.84	7	S	U	6.27	8
18	Butyl alcohol, tertiary	S	Y	17.6	8	S	U-V	6.27–8.84	14	S	Z1	27.0	7	S	Z	22.7	8
19	Butyl butyrate	S	X	12.9	8	S	N	3.40	12	S	V	8.84	7	S	Y	17.6	8
20	Butyl Carbitol	LS	X	12.9	11	LS	Q	4.35	18+	S	X	12.9	6	S	X	12.9	11
21	Butyl Cellosolve	S	U	6.27	7	S	H	2.00	14	LS				LS			
22	Butyl ether	SW				SW				SLS				I			
23	Butyl lactate	LS	V	8.84	9	LS	P	4.00	18+	S	Z1	27.0	7-8	S	Y	17.6	7-8
24	Butyl propionate	LS	R	4.70	7	LS	E	1.25	14	S				LS	M	3.20	9
25	Carbitol	S				S				LS				LS			
26	Carbitol acetate	I				I				I				I			
27	Carbon disulfide	GL				SLS				LS				LS			
28	Carbon tetrachloride	SW				SW				SW				SW			
29	Cellosolve	S	T	5.50	10	S	A	0.50	15	S	U	6.27	7	S	T	5.50	9
30	Cellosolve acetate	S	S	5.00	9	S	H	2.00	15	S	U	6.27	8	S	U	6.27	8
31	Chlorbenzol	GL				GL				GL				GL			
32	Chloroform	GL				GL				TVG				TVG			
33	Coal tar naphtha	I				I				SW				SW			
34	Denatured alcohol No. 1	S				S				S				S			
35	Denatured alcohol No. 5	S				S				S				S			
36	Diacetone alcohol	S	Z	22.7	11	S	H	2.00	15	S	Z	22.7	8	S	V	8.84	10
37	Dibutyl phthalate	SW				SW				SW				SLS			
38	Dichloroethyl ether	SW				SW				SW				SW			
39	Diethyl carbonate	SW				SW				SW				SW			
40	Diethylene glycol	SLS				SLS				SLS				SLS			
41	Diethylene glycol butyl ether	LS	X	12.9	11	LS	Q	4.35	18+	S	X	12.9	6	S	X	12.9	11
42	Diethylene glycol ethyl ether	S				S				LS				LS			
43	Diethylene glycol ethyl ether acetate	I				I				I				I			
44	Diethylene glycol methyl ether	S	V	8.84	9	S	M	3.20	13	S	W-X	10.70–12.9	9	S	W	10.70	9
45	Diethylene glycol monoacetate																

* All determinations made with

S Soluble, 90–100% of resin dissolved.
LS Largely soluble, 50–90% of resin dissolved.
PS Partly soluble, 25–50% of resin dissolved.
SLS Slightly soluble, 5–25% of resin dissolved.
I Insoluble, resin unaffected by solvent.

*(Continued)**

Mastic				Philippine Manila Bold Pale Chips				Pontianak Bold Scraped				Sandarac				Singapore Damar No. 1				
Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	
PS				S	X	12.9	12	I				PS				PS				1
PS				S	A	0.50	8	S	R	4.70	5	S				PS				2
S	T-U	5.50–6.27	8	SW				SW				NF				S				3
S				S	U	6.27	8	S	Y	17.6	5	S				S				4
S	A–	–0.50	6	S	Y	17.6	7	S	Z1	27.0	6	LS	Z	22.7	8	S	A–	–0.50	4	5
S				S	U	6.27	11	S	Z	22.7	9	S	V	8.84	8	LS				6
LS	A–	–0.50	6	S	U	6.27	9	S	Y	17.6	5	LS	O	3.70	7	LS				7
S	I-J	2.25–2.50	7	S	X-Y	12.9–17.6	9	S				S	Y	17.6	8	LS	N	3.40	WC	8
S	A–	–0.50	10	SW				SW				I				S				9
S	E	1.25	17	LS	Z1	27.0	18+	S	Z4	63.4	18	LS	Z3	46.3	18+	NF				10
S	A–	–0.50	6	S	A	0.50	11	S	L	3.00	9	S	D-E	1.00–1.25	7	PS				11
S				GL				SW				PS				S				12
S	F	1.40	7	LS	Z1	27.0	12	S	Z6	148.0	8	S	Z3	46.3	9	LS				13
S				S	T	5.50	9	S	Y	17.6	4	S				LS				14
S	A–	–0.50	6	S	O	3.70	9	S	V-W	8.84–10.70	6	S	U	6.27	8	LS	A–	–0.50		15
S				S	N	3.40	11	S	X	12.9	9	S				PS				16
S	B	0.65	5	S	U	6.27	7	S	Y	17.6	7	S	T	5.50	8	PS				17
S	J	2.50	7	S	Z–Z1	22.7–27.0	7	S	Z	22.7	6	S	Z1	27.0	8	PS				18
S				S	V	8.84	9	S	Z4	63.4	6	I				LS				19
LS	C	0.85	6	S	E	1.25	8	LS	Z2	36.2	6	S	Y	17.6	7	LS				20
S				LS				LS				S				PS				21
LS	A–	–0.50	5	I				SW				SLS				S				22
LS	C	0.85	7	LS	Z1	27.0	10	S	Z3	46.3	7	PS				LS				23
S				S	X	12.9	6	LS	Z1	27.0	6	I				S				24
S				S				S	Z2	36.2	7	S				PS				25
S				I				S	Z5	98.5	6	GL				PS				26
S	A–	–0.50	6	S			8	NF				NF				S	A–	–0.50	7	27
PS				SW				SW				I				PS				28
S	A–	–0.50	6	S	J	2.50	12	S	X-Y	12.9–17.6	9	S	P	4.00	7	PS				29
S	A–	–0.50	5	S	U	6.27	7	LS				S	W	10.70	7	PS				30
S	A–	–0.50	7	GL				SW				TVG				S				31
PS				S			9	NF				PS				S	D	1.00	6	32
S				SW				SW				SLS				S				33
LS	A–	–0.50	6	S	M	3.20	6	PS				S	F	1.40	7	PS				34
LS	A–	–0.50	6	S	I	2.25	13	PS				S	G–H	1.65–2.00	7	PS				35
S				S	Y	17.6	12	S	Z	22.7	9	S				SLS				36
S				SW				SLS				SLS				LS				37
S	E	1.25	7	SW				SW				I				PS				38
S	A–	–0.50	6	SW				SW				I				PS				39
SLS				SLS				PS				I				I				40
LS	C	0.85	6	S	E	1.25	8	LS	Z2	36.2	6	S	Y	17.6	7	LS				41
S				S				S	Z2	36.2	7	S				PS				42
S				I				S	Z5	98.5	6	GL				PS				43
S				S	X	12.9	8	S	Z4–Z5	63.4–98.5	7	GL				PS				44
SLS												I				PS				45

100 g. of resin and 100 g. of solvent.

SW Swelled, resin so affected by solvent.
TVG Transparent viscous gel formed.
GL Gelatinous liquid resulted.
NF Non-flowing gel.
WC White and cloudy.

TABLE XIX

		Accroides				Batavia Damar							
						A/D				A/E			
		Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color
46	Diethylene oxide	LS				PS	A	0.50	3	PS	A	0.50	3
47	Dimethyl phthalate	PS				SW				SW			
48	Dioxane	LS				PS	A	0.50	3	PS	A	0.50	3
49	Dipentene	PS				S	A	0.50	4	S	A	0.50	4
50	Ethyl abietate	LS				SW				SW			
51	Ethyl acetate	LS				LS	A−	−0.50	3	LS	A−	−0.50	3
52	Ethyl alcohol	S				PS				PS			
53	2-Ethyl butyl acetate	PS				LS				LS			
54	2-Ethyl butyl alcohol	LS				LS				LS			
55	Ethyl ether	LS				S	A−	−0.50	3	S	A−	−0.50	2
56	2-Ethyl hexyl acetate	LS				S	A	0.50	3	S	A	0.50	3
57	2-Ethyl hexyl alcohol	PS				LS				LS			
58	Ethylene dichloride	SLS				S				S			
59	Ethylene glycol butyl ether	LS				PS				PS			
60	Ethylene glycol diethyl ether					PS				PS			
61	Ethylene glycol ethyl ether	LS				PS				PS			
62	Ethylene glycol ethyl ether acetate	S	E	1.25	18+	PS				PS			
63	Ethylene glycol isoamyl ether					PS				PS			
64	Ethylene glycol isobutyl ether					PS				PS			
65	Ethylene glycol isopropyl ether					PS				PS			
66	Ethylene glycol methyl ether	LS				PS				PS			
67	Ethylene glycol methyl ether acetate	LS				SLS				SLS			
68	Ethylene glycol propyl ether					PS				PS			
69	Glycol diacetate	S	R	4.70	18+	I				I			
70	Glycol ether acetate	S	E	1.25	18+	PS				PS			
71	Glycol monoacetate					I				I			
72	Heptyl acetate, secondary					LS				LS			
73	Heptyl alcohol, secondary					LS				LS			
74	Hercosol 80	I				S	E	1.25	4	S	E	1.25	3
75	Hexalin	PS				GL				GL			
76	Hexone	LS				PS				PS			
77	Hexyl acetate, secondary					LS				LS			
78	Hexyl alcohol, normal	PS				LS				LS			
79	Hexyl alcohol, secondary					SLS				SLS			
80	Isopropyl acetate	LS				S				S	A−	−0.50	5
81	Isopropyl alcohol	LS				PS	A−	−0.50	4	PS	A	0.50	4
82	Isopropyl alcohol 91%	S	D	1.00	18+	PS				PS			
83	Isopropyl alcohol 95%	S	D	1.00	18+	PS				PS			
84	Isopropyl alcohol 98%	S	D	1.00	18+	PS				PS			
85	Isopropyl ether	SLS				S				S			
86	Linoleic acid	SLS				LS				LS			
87	Mesityl oxide	S	A	0.50	18+	S	A−	−0.50	3-4	S	A−	−0.50	3
88	Methyl acetate 82%	LS				SLS				SLS			

* All determinations made with

S Soluble, 90–100% of resin dissolved.
LS Largely soluble, 50–90% of resin dissolved.
PS Partly soluble, 25–50% of resin dissolved.
SLS Slightly soluble, 5–25% of resin dissolved.

(*Continued*)*

Batavia Damar "E" Seeds Solubility	Viscosity	Poises	Color	Batavia Damar Dust Solubility	Viscosity	Poises	Color	Batu East India Nubs and Chips Solubility	Viscosity	Poises	Color	Black East India Bold Scraped Solubility	Viscosity	Poises	Color	Boea Hard Bold Amber Solubility	Viscosity	Poises	Color	
PS				PS				SW				SW				GL				46
SW				SW				SW				SW				SW				47
PS				PS				SW				SW				GL				48
S				S				S	Z6	148.0	17	S	Z2	36.2	15	GL				49
SW				SW				I				SW				SW				50
LS				LS				I				I				GL				51
PS				PS				PS				PS				LS				52
LS				LS				NF				I				GL				53
LS				LS				NF				I				S				54
S				S				SW				GL				GL				55
S				S				SW				S	Z2	36.2	15	GL				56
LS				LS				LS				I				S				57
S				S				NF				TVG				GL				58
PS				PS				SW				SW				S				59
PS				PS																60
PS				PS				SW				I				GL				61
PS				PS				S	H	2.00	18+	SLS				S	Y-Z	17.6–22.7	4	62
PS				PS																63
PS				PS																64
PS				PS																65
PS				PS				PS				I				GL				66
SLS				SLS				PS				I				S				67
PS				PS																68
I				I				I				I				SLS				69
PS				PS				S	H	2.00	18+	SLS				S	Y-Z	17.6–22.7	4	70
I				I																71
LS				LS								LS				PS				72
LS				LS								LS				PS				73
S				S				SW				SW				GL				74
GL				GL				SW				SW				GL				75
PS				PS				PS				I				S				76
LS				LS				LS				LS				PS				77
LS				LS				NF				I				S				78
SLS				SLS								PS				LS				79
S	A–	–0.50	9	S	A–	–0.50	10	SLS				PS				PS				80
PS				PS				I				I				S	Y	17.6	6	81
PS				PS				PS				SLS				LS				82
PS				PS				PS				SLS				LS				83
PS				PS				PS				SLS				S	Y	17.6	6	84
S				S				I				SW				GL				85
LS				LS				SW				SLS				SLS				86
S	A–	–0.50	9	S	A–	–0.50	9	PS				SLS				S	O	3.70	2-3	87
SLS				SLS				SW				I				S				88

* 100 g. of resin and 100 g. of solvent.

I Insoluble, resin unaffected by solvent.
SW Swelled, resin so affected by solvent.
TVG Transparent viscous gel formed.
GL Gelatinous liquid resulted.
NF Non-flowing gel.

TABLE XIX

		Accroides				Batavia Damar							
						A/D				A/E			
		Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color
46	Diethylene oxide	LS				PS	A	0.50	3	PS	A	0.50	3
47	Dimethyl phthalate	PS				SW				SW			
48	Dioxane	LS				PS	A	0.50	3	PS	A	0.50	3
49	Dipentene	PS				S	A	0.50	4	S	A	0.50	4
50	Ethyl abietate	LS				SW				SW			
51	Ethyl acetate	LS				LS	A−	−0.50	3	LS	A−	−0.50	3
52	Ethyl alcohol	S				PS				PS			
53	2-Ethyl butyl acetate	PS				LS				LS			
54	2-Ethyl butyl alcohol	LS				LS				LS			
55	Ethyl ether	LS				S	A−	−0.50	3	S	A−	−0.50	2
56	2-Ethyl hexyl acetate	LS				S	A	0.50	3	S	A	0.50	3
57	2-Ethyl hexyl alcohol	PS				LS				LS			
58	Ethylene dichloride	SLS				S				S			
59	Ethylene glycol butyl ether	LS				PS				PS			
60	Ethylene glycol diethyl ether					PS				PS			
61	Ethylene glycol ethyl ether	LS				PS				PS			
62	Ethylene glycol ethyl ether acetate	S	E	1.25	18+	PS				PS			
63	Ethylene glycol isoamyl ether					PS				PS			
64	Ethylene glycol isobutyl ether					PS				PS			
65	Ethylene glycol isopropyl ether					PS				PS			
66	Ethylene glycol methyl ether	LS				PS				PS			
67	Ethylene glycol methyl ether acetate	LS				SLS				SLS			
68	Ethylene glycol propyl ether					PS				PS			
69	Glycol diacetate	S	R	4.70	18+	I				I			
70	Glycol ether acetate	S	E	1.25	18+	PS				PS			
71	Glycol monoacetate					I				I			
72	Heptyl acetate, secondary					LS				LS			
73	Heptyl alcohol, secondary					LS				LS			
74	Hercosol 80	I				S	E	1.25	4	S	E	1.25	3
75	Hexalin	PS				GL				GL			
76	Hexone	LS				PS				PS			
77	Hexyl acetate, secondary					LS				LS			
78	Hexyl alcohol, normal	PS				LS				LS			
79	Hexyl alcohol, secondary					SLS				SLS			
80	Isopropyl acetate	LS				S				S	A−	−0.50	5
81	Isopropyl alcohol	LS				PS	A−	−0.50	4	PS	A	0.50	4
82	Isopropyl alcohol 91%	S	D	1.00	18+	PS				PS			
83	Isopropyl alcohol 95%	S	D	1.00	18+	PS				PS			
84	Isopropyl alcohol 98%	S	D	1.00	18+	PS				PS			
85	Isopropyl ether	SLS				S				S			
86	Linoleic acid	SLS				LS				LS			
87	Mesityl oxide	S	A	0.50	18+	S	A−	−0.50	3–4	S	A−	−0.50	3
88	Methyl acetate 82%	LS				SLS				SLS			

* All determinations made with

S Soluble, 90–100% of resin dissolved.
LS Largely soluble, 50–90% of resin dissolved.
PS Partly soluble, 25–50% of resin dissolved.
SLS Slightly soluble, 5–25% of resin dissolved.

*(Continued)**

Batavia Damar								Batu East India Nubs and Chips				Black East India Bold Scraped				Boea Hard Bold Amber				
"E" Seeds				Dust																
Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	
PS				PS				SW				SW				GL				46
SW				SW				SW				SW				SW				47
PS				PS				SW				SW				GL				48
S				S				S	Z6	148.0	17	S	Z2	36.2	15	GL				49
SW				SW				I				SW				SW				50
LS				LS				I				I				GL				51
PS				PS				PS				PS				LS				52
LS				LS				NF				I				GL				53
LS				LS				NF				I				S				54
S				S				SW				GL				GL				55
S				S				SW				S	Z2	36.2	15	GL				56
LS				LS				LS				I				S				57
S				S				NF				TVG				GL				58
PS				PS				SW				SW				S				59
PS				PS																60
PS				PS				SW				I				GL				61
PS				PS				S	H	2.00	18+	SLS				S	Y-Z	17.6–22.7	4	62
PS				PS																63
PS				PS																64
PS				PS																65
PS				PS				PS				I				GL				66
SLS				SLS				PS				I				S				67
PS				PS																68
I				I				I				I				SLS				69
PS				PS				S	H	2.00	18+	SLS				S	Y-Z	17.6–22.7	4	70
I				I																71
LS				LS								LS				PS				72
LS				LS								LS				PS				73
S				S				SW				SW				GL				74
GL				GL				SW				SW				GL				75
PS				PS				PS				I				S				76
LS				LS				LS				LS				PS				77
LS				LS				NF				I				S				78
SLS				SLS								PS				LS				79
S	A–	–0.50	9	S	A–	–0.50	10	SLS				PS				PS				80
PS				PS				I				I				S	Y	17.6	6	81
PS				PS				PS				SLS				LS				82
PS				PS				PS				SLS				LS				83
PS				PS				PS				SLS				S	Y	17.6	6	84
S				S				I				SW				GL				85
LS				LS				SW				SLS				SLS				86
S	A–	–0.50	9	S	A–	–0.50	9	PS				SLS				S	O	3.70	2-3	87
SLS				SLS				SW				I				S				88

100 g. of resin and 100 g. of solvent.

I Insoluble, resin unaffected by solvent.
SW Swelled, resin so affected by solvent.
TVG Transparent viscous gel formed.
GL Gelatinous liquid resulted.
NF Non-flowing gel.

TABLE XIX

		Congo															
		No. 1 Water-white				No. 4 Pale Bold Straw				No. 11 H.D. Amber Bold				No. 21 Selected Nubs			
		Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color
46	Diethylene oxide	GL				SW				SW				SW			
47	Dimethyl phthalate	I				SW				SW				I			
48	Dioxane	GL				SW				SW				SW			
49	Dipentene	I				SW				SW				SW			
50	Ethyl abietate	SW				SW				SW				SW			
51	Ethyl acetate	GL				TVG				SW				TVG			
52	Ethyl alcohol	I				I				I				I			
53	2-Ethyl butyl acetate	TVG				TVG				TVG				TVG			
54	2-Ethyl butyl alcohol	TVG				TVG				TVG				TVG			
55	Ethyl ether	I				SW				SW				TVG			
56	2-Ethyl hexyl acetate	SW				SW				SW				SW			
57	2-Ethyl hexyl alcohol	TVG				TVG				TVG				TVG			
58	Ethylene dichloride	SW				SW				SW				SW			
59	Ethylene glycol butyl ether	SLS				SLS				SLS				SLS			
60	Ethylene glycol diethyl ether	SLS				SLS				SLS				SLS			
61	Ethylene glycol ethyl ether	GL				TVG				SW				SW			
62	Ethylene glycol ethyl ether acetate	GL				GL				GL				GL			
63	Ethylene glycol isoamyl ether	SLS				SLS				SLS				SLS			
64	Ethylene glycol isobutyl ether	SLS				SLS				SLS				SLS			
65	Ethylene glycol isopropyl ether	SLS				SLS				SLS				SLS			
66	Ethylene glycol methyl ether	SLS				SLS				SLS				SLS			
67	Ethylene glycol methyl ether acetate	TVG				TVG				TVG				TVG			
68	Ethylene glycol propyl ether	SLS				SLS				SLS				SLS			
69	Glycol diacetate	I				I				I				I			
70	Glycol ether acetate	GL				GL				GL				GL			
71	Glycol monoacetate	I				I				I				I			
72	Heptyl acetate, secondary	PS				PS				I				PS			
73	Heptyl alcohol, secondary	PS				PS				PS				PS			
74	Hercosol 80	SW				SW				SW				SW			
75	Hexalin	GL				SW				SW				SW			
76	Hexone	TVG				TVG				TVG				TVG			
77	Hexyl acetate, secondary	TVG				PS				SLS				SLS			
78	Hexyl alcohol, normal	TVG				TVG				TVG				TVG			
79	Hexyl alcohol, secondary	PS				PS				PS				PS			
80	Isopropyl acetate	SLS				SLS				SLS				SLS			
81	Isopropyl alcohol	GL				TVG				SW				TVG			
82	Isopropyl alcohol 91%	PS				PS				PS				PS			
83	Isopropyl alcohol 95%	PS				PS				PS				PS			
84	Isopropyl alcohol 98%	PS				PS				PS				PS			
85	Isopropyl ether	I				I				I				I			
86	Linoleic acid	I				I				I				I			
87	Mesityl oxide	GL				GL				GL				TVG			
88	Methyl acetate 82%	GL				PS				TVG				GL			

* All determinations made with

S Soluble, 90–100% of resin dissolved.
LS Largely soluble, 50–90% of resin dissolved.
PS Partly soluble, 25–50% of resin dissolved.
SLS Slightly soluble, 5–25% of resin dissolved.
NF Non-flowing gel.

*(Continued)**

Congo Ester				East India Macassar								East India Singapore								
				Bold				Nubs				Bold				Nubs				
Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	
S	M	3.20	18+	PS				PS	B	0.65	12	PS				PS				46
SLS				I				SW				I				SW				47
S	M	3.20	18+	PS				PS	B	0.65	12	I				SW				48
S	N	3.40	17	S				S	Q	4.35	10	S				S	Y	17.6	13	49
GL				I				I				I				SW				50
S	B	0.65	18+	I				I				I				I				51
I				SLS				SLS				SLS				SLS				52
S	H	2.00	18+	PS				PS				PS				PS				53
S	X	12.9	18+	SLS				SLS				SLS				SLS				54
S	A−	−0.50	18+	LS				LS	A−	−0.50	10	SLS				GL				55
S	R	4.70	18+	SLS				SLS				S				S	Z1	27.0	14	56
S	Z1	27.0	18+	I				I				I				I				57
S	L	3.00	18+	S				S				S				S				58
S	U	6.27	18+	PS				PS				PS				PS				59
																				60
SLS				I				I				I				I				61
SLS				I				I				I				I				62
																				63
																				64
																				65
SLS				I				I				I				I				66
SLS				I				I				I				I				67
																				68
I				SLS				SLS				SLS				SLS				69
SLS				I				I				I				I				70
																				71
				PS				PS				PS				PS				72
				PS				PS				PS				PS				73
S	V–W	8.84–10.7	18+	LS				LS	Z6	148.0	12	I				SW				74
PS				I				SW				I				SW				75
S	E	1.25	18+	I				I				I				I				76
				LS				LS				LS				LS				77
S	X	12.9	18+	PS				PS				I				I				78
												PS				PS				79
S	D	1.00	18+	I				I				SLS				I				80
SLS				I				I				I				I				81
SLS								SLS				SLS				SLS				82
SLS								SLS				SLS				SLS				83
SLS				SLS				SLS				SLS				SLS				84
S	B	0.65	18+	S				S				PS				S				85
S	Z1	27.0	18+	LS				LS				LS				LS				86
S				PS				PS				LS				LS				87
PS				I				SW				I				SW				88

100 g. of resin and 100 g. of solvent.

I Insoluble, resin unaffected by solvent.
SW Swelled, resin so affected by solvent.
TVG Transparent viscous gel formed.
GL Gelatinous liquid resulted.

TABLE XIX

No.	Solvent	Elemi Solubility	Elemi Viscosity	Elemi Poises	Elemi Color	Kauri Pale No. 2 Solubility	Kauri Pale No. 2 Viscosity	Kauri Pale No. 2 Poises	Kauri Pale No. 2 Color	Kauri Brown No. 2 Solubility	Kauri Brown No. 2 Viscosity	Kauri Brown No. 2 Poises	Kauri Brown No. 2 Color	Manila WS Solubility	Manila WS Viscosity	Manila WS Poises
46	Diethylene oxide	S	A−	−0.50	1	S	Y	17.6	12	S	Z2	36.2	18	S	P	4.00
47	Dimethyl phthalate	PS				SW				SW				SW		
48	Dioxane	S	A−	−0.50	1	S	Y	17.6	12	S	Z2	36.2	18	S	P	4.00
49	Dipentene	PS				I				I				I		
50	Ethyl abietate	SLS				I				I				SW		
51	Ethyl acetate	PS				S	R	4.70	12	S	U	6.27	18	S		
52	Ethyl alcohol	SLS				S	V	8.84	13	S	W	10.70	18	S		
53	2-Ethyl butyl acetate	S				S	Z1	27.0	12	S	Z3	46.3	18+	S	Z3	46.3
54	2-Ethyl butyl alcohol	S				S	Z3	46.3	12	S	Z2	36.2	18+	S	Z	22.7
55	Ethyl ether	S				LS	A−	−0.50	8	GL				LS		
56	2-Ethyl hexyl acetate	PS				PS	Z3	46.3	10	SW				PS		
57	2-Ethyl hexyl alcohol	S				LS				S	Z3	46.3	18	S	Z1-Z2	27.0-36.2
58	Ethylene dichloride	PS				S				LS				LS		
59	Ethylene glycol butyl ether	S				S	W	10.70	14	S	Z2	36.2	18+	LS	K-L	2.75-3.00
60	Ethylene glycol diethyl ether	S												SW		
61	Ethylene glycol ethyl ether	PS				S	Z	22.7	12	S	X	12.9	18	S	O	3.70
62	Ethylene glycol ethyl ether acetate	PS				S	Y	17.6	12	S	Z-Z1	22.7-27 0	17	S	V-W	8.84-10.70
63	Ethylene glycol isoamyl ether	S												SW		
64	Ethylene glycol isobutyl ether	S												SW		
65	Ethylene glycol isopropyl ether	S												SW		
66	Ethylene glycol methyl ether	PS				S	Y	17.6	12	S	Z	22.7	18+	SW		
67	Ethylene glycol methyl ether acetate	S				S	Z	22.7	12	S	Z2	36.2	18+	S	Z	22.7
68	Ethylene glycol propyl ether	S												SW		
69	Glycol diacetate	S				SLS				SLS				SLS		
70	Glycol ether acetate	SLS				S	Y	17.6	12	S	Z-Z1	22.7-27.0	17	S	V-W	8.84-10.70
71	Glycol monoacetate	S												I		
72	Heptyl acetate, secondary									SLS				PS		
73	Heptyl alcohol, secondary									PS				PS		
74	Hercosol 80	LS	A−	−0.50	2	PS	Z5	98.5	11	TVG				SLS		
75	Hexalin	LS	D	1.00	1	SLS				TVG				GL		
76	Hexone	S				S	U	6.27	12	S	V-W	8.84-10.70	18+	S	P	4.00
77	Hexyl acetate, secondary									PS				PS		
78	Hexyl alcohol, normal	S				S	Z3	46.3	12	S	Z2	36.2	18+	S	Z	22.7
79	Hexyl alcohol, secondary					LS				LS				PS		
80	Isopropyl acetate	S				LS	Q-R	4.35-4.70	12	S	W	10.70	18+	S	Q-R	4.35-4.70
81	Isopropyl alcohol	PS				S	B	0.65	12	S	X	12.9	18	S	M	3.20
82	Isopropyl alcohol 91%					S	X	12.9	12	LS				LS		
83	Isopropyl alcohol 95%					S	X	12.9	12	LS				LS		
84	Isopropyl alcohol 98%					S	X	12.9	12	LS				LS	M	3.20
85	Isopropyl ether	PS				SW				I				PS		
86	Linoleic acid	S	E	1.25	5	SLS				I				LS		
87	Mesityl oxide	S	A−	−0.50		S	Q-R	4.35-4.70	11-12	S	N	3.40	18+	LS		
88	Methyl acetate 82%	LS				S	E-F	1.25-1.40	12	S	H	2.00	18	S	C	0.85

* All determinations made with

S Soluble, 90–100% of resin dissolved.
LS Largely soluble, 50–90% of resin dissolved.
PS Partly soluble, 25–50% of resin dissolved.
SLS Slightly soluble, 5–25% of resin dissolved.
NF Non-flowing gel.

(*Continued*)*

Manila MA												Manila Loba				DK				
Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	
S	P	4.00	8	LS				LS				LS				LS	K	2.75	12	46
SW				SW				SW				SW				SW				47
S	P	4.00	8	LS				LS				LS				LS	K	2.75	12	48
I				PS				I				I				I				49
SW				SW				SW				SW				SW				50
S				S				S	L	3.00	4	S				S				51
S				S	E	1.25	6	S	I	2.25	6	S	G–H	1.65–2.00	7	S	B–C	0.65–0.85	11	52
S	Z	22.7	8	S	Z	22.7	6	S	Z1–Z2	27.0 36.2	6	LS				S	X	12.9	11	53
S	X	12.9	8	S	X	12.9	5	S	X–Y	12.9–17.6	6	S	Y	17.6	6	S	V	8.84	11	54
LS				S				S	C	0.85	4	S				S				55
S	V–W	8.84–10.70	9	S	V	8.84	5	S	Y	17.6	5	LS				S	T	5.50	10	56
S	Z1	27.0	9	S	Z3	46.3	5	S	Y	17.6	6	LS				S	Y	17.6	11	57
LS				LS				LS				PS				PS				58
LS	K–L	2.75–3.00	9	S	S	5.00	6	S	X	12.9	5	S	X	12.9	7	S	U	6.27	9	59
SW																				60
S	O	3.70	12	S	U	6.27	5	S	U	6.27	6	S	R	4.70	11	S	I	2.25	12	61
S	V	8.84	10	S	W	10.70	5	S	V	8.84	6	LS				S	S	5.00	11	62
SW																				63
SW																				64
SW																				65
SW				LS				LS				LS				LS				66
S	U	6.27	8	S	V–W	8.84–10.70	5	S	V	8.84	6	S	U	6.27	6	S	N	3.40	11	67
SW																				68
SLS				SLS				SLS				SLS				SLS				69
S	V	8.84	10	S	W	10.70	5	S	V	8.84	6	LS				S	S	5.00	11	70
I																				71
PS				PS				PS				PS				PS				72
PS				PS				PS				PS				PS				73
SLS				PS				GL				SLS				PS				74
GL				PS				GL				PS				PS				75
S	P	4.00	9	S	S	5.00	5	S	P	4.00	6	S	S	5.00	6	S	I	2.25	8	76
PS				PS				PS				PS				PS				77
S	X	12.9	8	S	X	12.9	5	S	X–Y	12.9–17.6	6	S	Y	17.6	6	S	V	8.84	11	78
PS				LS				LS				LS				LS				79
S	Q–R	4.35–4.70	6	S	I–J	2.25–2.50	6	LS				LS	M	3.20	7	LS	G	1.65	9	80
S	N	3.40	12	S	T	5.50	5	S	T	5.50	6	S	M	3.20	11	S	H	2.00	12	81
LS				LS				LS				LS				LS				82
LS				LS				LS				LS				LS				83
LS	N	3.40	12	LS	T	5.50	5	LS	T	5.50	6	LS	M	3.20	11	LS	H	2.00	12	84
PS				PS				PS				PS				PS				85
LS				LS				LS				LS				LS				86
LS				LS				LS				LS				LS				87
S	B	0.65	9	S	B	0.65	5	S	C	0.85	6	S	D	1.00	8	S	A–	–0.50	8	88

* 100 g. of resin and 100 g. of solvent.

I Insoluble, resin unaffected by solvent.
SW Swelled, resin so affected by solvent.
TVG Transparent viscous gel formed.
GL Gelatinous liquid resulted.

TABLE XIX

		Manila Loba (continued)								Manila							
		CNE				Dust				CBB				DBB			
		Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color
46	Diethylene oxide	LS	G-H	1.65-2.00	8	S	F	1.40	14	S	Q	4.35	4	S	T	5.50	8
47	Dimethyl phthalate	SW				SW				SW				SW			
48	Dioxane	LS	G-H	1.65-2.00	8	S	F	1.40	14	S	Q	4.35	4	S	T	5.50	8
49	Dipentene	I				I				SLS				I			
50	Ethyl abietate	SW				SW				SW				SW			
51	Ethyl acetate	S				S				S	G	1.65	6	S	B	0.65	9
52	Ethyl alcohol	S	G	1.65	7	S	A–	–0.50	15	S				S			
53	2-Ethyl butyl acetate	S	Z	22.7	7	S	V	8.84	15	S	X-Y	12.9-17.6	7	S	Z1	27.0	8
54	2-Ethyl butyl alcohol	S	X	12.9	8	S	S	5.00	15	S	X-Y	12.9-17.6	7	S	Y	17.6	8
55	Ethyl ether	S				S				S	E	1.25	4	S	A	0.50	8
56	2-Ethyl hexyl acetate	S	W	10.70	8	S	I	2.25	12	S	V	8.84	7	S	U	6.27	7
57	2-Ethyl hexyl alcohol	S	X-Y	12.9-17.6	8	S	W	10.70	15	LS				S	Z2	36.2	8
58	Ethylene dichloride	PS				LS				LS	Z3	46.3	9	PS			
59	Ethylene glycol butyl ether	S	U	6.27	7	S	H	2.00	14	LS				LS			
60	Ethylene glycol dibutyl ether																
61	Ethylene glycol ethyl ether	S	T	5.50	10	S	A	0.50	15	S	U	6.27	7	S	T	5.50	9
62	Ethylene glycol ethyl ether acetate	S	S	5.00	9	S	H	2.00	15	S	U	6.27	8	S	U	6.27	8
63	Ethylene glycol [illegible] ether																
64	Ethylene glycol isobutyl ether																
65	Ethylene glycol isopropyl ether																
66	Ethylene glycol methyl ether	LS				LS				S	N	3.40	8	S	X	12.9	8
67	Ethylene glycol methyl ether acetate	S	U	6.27	8	S	F	1.40	12	S	V	8.84	8	S	U-V	6.27-8.84	9
68	Ethylene glycol propyl ether																
69	Glycol diacetate	SLS				SLS				SLS				SLS			
70	Glycol ether acetate	S	S	5.00	9	S	H	2.00	15	S	U	6.27	8	S	U	6.27	8
71	Glycol monoacetate																
72	Heptyl acetate, secondary	PS				PS				PS				PS			
73	Heptyl alcohol, secondary	PS				PS				PS				LS			
74	Hercosol 80	PS				SW				PS	Z1	27.0	6	GL			
75	Hexalin	LS	Z3	46.3	12	PS				PS				LS			
76	Hexone	S	K	2.75	7	S	A–	–0.50	12	S	J	2.50	7	S	R	4.70	8
77	Hexyl acetate, secondary	PS				PS				PS				PS			
78	Hexyl alcohol, normal	S	X	12.9	8	S	S	5.00	15	S	X-Y	12.9-17.6	7	S	Y	17.6	8
79	Hexyl alcohol, secondary	LS				LS				LS				LS			
80	Isopropyl acetate	PS				S	A–	–0.50	13	S	H	2.00	8	LS			
81	Isopropyl alcohol	S	M	3.20	9	S	A	0.50	18+	S	O	3.70	8	S	L	3.00	9
82	Isopropyl alcohol 91%	LS				LS				LS				LS			
83	Isopropyl alcohol 95%	LS				LS				LS				LS			
84	Isopropyl alcohol 99%	LS	M	3.20	9	LS	A	0.50	18+	LS	O	3.70	8	S	L	3.00	9
85	Isopropyl ether	PS				PS				SW				SW			
86	Linoleic acid	LS				LS				LS				LS			
87	Mesityl oxide	LS				LS				LS				LS			
88	Methyl acetate 82%	S	D	1.00	7	S	A–	–0.50	13	S	D	1.00	7	S	B	0.65	8

* All determinations made with

S Soluble, 90–100% of resin dissolved.
LS Largely soluble, 50–90% of resin dissolved.
PS Partly soluble, 25-50% of resin dissolved.
SLS Slightly soluble, 5-25% of resin dissolved.
NF Non-flowing gel.

*(Continued)**

Mastic				Philippine Manila Bold Pale Chips				Pontianak Bold Scraped				Sandarac				Singapore Damar No. 1				
Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	
S	A–	–0.50	6	S	V	8.84	7	S	Z2	36.2	5	S	W	10.70	7	PS				46
PS				I				SW				GL				SW				47
S	A–	–0.50	6	S	V	8.84	7	S	Z2	36.2	5	S	W	10.70	7	PS				48
LS	A	0.50	5	I				SW				I				S				49
SW				I				SW				TVG				SW				50
S				S	X	12.9	11	S	W	10.70	4	S				PS				51
S				S				S				S				PS				52
S	Z2	36.2	4	S				S	Z3	46.3	5	LS				LS				53
S				S	Y	17.6	7	S	Z3	46.3	5	S				LS				54
S	A–	–0.50	6	S	C	0.85	7	S	R	4.70	4	PS				S				55
S	A–	–0.50	6	LS	Z5	98.5	10	SW				LS				S				56
S	M	3.20	6	S	Z2	36.2	6	LS				LS				LS				57
S	A–	–0.50	6	NF				PS				SLS				S				58
S				LS				LS				S				PS				59
S												I				PS				60
S	A–	–0.50	6	S	J	2.50	12	S	X–Y	12.9–17.6	9	S	P	4.00	7	PS				61
S	A–	–0.50	5	S	U	6.27	7	LS				S	W	10.70	7	PS				62
S												S				PS				63
S																PS				64
S																PS				65
S				S	U	6.27	3	S	X	12.9	8	S				PS				66
S				S	Y	17.6	3	S	Z1	27.0	8	S				SLS				67
S												S				PS				68
SLS								SLS				I				I				69
S	A–	–0.50	6	S	U	6.27	7	LS				S	W	10.70	7	PS				70
SLS												I				I				71
								SLS								LS				72
								LS								LS				73
LS	B	0.65	5	PS	Z3	46.3	10	SW				SLS				S				74
PS				LS	Z6	148.0	9	SLS				PS				S				75
S				S	P	4.00	7	S	V–W	8.84–10.70	5	S				PS				76
								PS								LS				77
S				S	Y	17.6	7	S	Z3	46.3	5	LS				LS				78
								S								SLS				79
S				S				S				S				PS				80
S	O	3.70	5	S	L	3.00	10	S	X	12.9	9	LS	E	1.25	7	PS				81
S				S				S				S				PS				82
S				S				S				S				PS				83
S	O	3.70	5	S	L	3.00	10	S	X	12.9	9	S	E	1.25	7	PS				84
LS	A–	–0.50	6	SW				SW				SLS				S				85
S	V–W	8.84–10.70	7	LS				PS				PS				S	Y	17.6	5	86
S	A–	–0.50	5–6	S	J	2.50	7–8	S	W	10.70	6–7	S	L	3.00	8	LS	A–	–0.50	4	87
S				S	A	0.50	8	S	J	2.50	7	S				PS				88

* 100 g. of resin and 100 g. of solvent.

I Insoluble, resin unaffected by solvent.
SW Swelled, resin so affected by solvent.
TVG Transparent viscous gel formed.
GL Gelatinous liquid resulted.

TABLE XIX

		Accroides				Batavia Damar							
						A D				A E			
		Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color
89	Methyl acetate	LS				LS	A−	−0.50	4	LS	A−	−0.50	3
90	Methyl alcohol	LS				I				I			
91	Methyl amyl acetate	PS				LS				LS			
92	Methyl amyl alcohol	PS				LS				LS			
93	Methyl n-amyl ketone	LS				PS				PS			
94	Methyl n-butyl ketone	S	A	0.50	18+	PS				PS			
95	Methyl Carbitol	PS				PS				PS			
96	Methyl Cellosolve	LS				PS				PS			
97	Methyl Cellosolve acetate	LS				SLS				SLS			
98	Methyl ethyl ketone	PS				PS	A−	−0.50	6	PS	A−	−0.50	6
99	Methyl isobutyl carbinol	PS				LS				LS			
100	Methyl isobutyl carbinol acetate	PS				LS				LS			
101	Methyl isobutyl ketone	LS				PS				PS			
102	Methyl propyl ketone	S	A−	−0.50	18+	LS	A−	−0.50	6	LS	A−	−0.50	6
103	Methyl salicylate	SLS				S	O	3.70	5	S	K	2.75	3
104	Nitrobenzol	PS				S				S	G	1.65	9
105	Octyl acetate	LS				S	A	0.50	3	S	A	0.50	3
106	Octyl alcohol	PS				LS				LS			
107	Petrohol					PS				PS			
108	Petroleum naphtha			See Special Chart on these solvents									
109	Phenol—60°C.	LS				GL				GL			
110	Phenol—25°C.	PS				NF				NF			
111	Phenyl Cellosolve	PS				TVG				TVG			
112	Propylene dichloride	PS				S				S			
113	Propylene glycol ethyl ether					PS				PS			
114	Propylene glycol isopropyl ether					PS				PS			
115	Propylene glycol methyl ether					PS				PS			
116	Shellacol	LS				PS	A−	−0.50	4	PS	A−	−0.50	4
117	Sodium hydroxide 10%	PS				SW				SW			
118	Solox	LS				PS	A−	−0.50	4	PS	A−	−0.50	4
119	Synasol	LS				PS				PS			
120	Terpineol	LS				S	Z	22.7	4	S	X	12.9	4
121	Tetrachlorethane	PS				S	W	10.70	5	S	V	8.84	5
122	Tetraethylene glycol					I				I			
123	Tetraethylene glycol ethyl ether					PS				PS			
124	Tetralin	I				S	I	2.25	17	S	G	1.65	17
125	Toluol	I				S	A	0.50	5	S	A−	−0.50	4
126	Trichlorethylene	SLS				S				S			
127	Tricresyl phosphate	PS				NF				NF			
128	Triethylene glycol	S				I				I			
129	Triethylene glycol ethyl ether					PS				PS			
130	Turpentine	SLS				S	O	3.70	5	S	K	2.75	5
131	Xylol	I				S	A	0.50	4	S	A−	−0.50	3

* All determinations made with

S Soluble, 90–100% of resin dissolved.
LS Largely soluble, 50–90% of resin dissolved.
PS Partly soluble, 25–50% of resin dissolved.
SLS Slightly soluble, 5–25% of resin dissolved.
NF Non-flowing gel.

*(Continued)**

Batavia Damar "E" Seeds Solubility	Viscosity	Poises	Color	Batavia Damar Dust Solubility	Viscosity	Poises	Color	Batu East India Nubs and Chips Solubility	Viscosity	Poises	Color	Black East India Bold Scraped Solubility	Viscosity	Poises	Color	Boea Hard Bold Amber Solubility	Viscosity	Poises	Color	
LS				LS				SW				I				LS	K	2.75	2	89
I				I				I				I				S	F	1.40	6	90
LS				LS				PS				I				GL				91
S	I	2.25	11	S	G-H	1.65-2.0	12	SW				I				S				92
PS				PS				LS				I				S				93
S	A−	−0.50	10	S	A−	−0.50	9	NF				PS				LS				94
PS				PS				PS				I				S				95
PS				PS								I				GL				96
SLS				SLS								I				S				97
PS				PS				SW				SLS				S				98
S	H-I	2.00-2.25	12	S	G	1.65	15	SW				I				S				99
LS				LS								I				GL				100
PS				PS								I				S				101
S	A−	−0.50	7	S	A−	−0.50	12	PS				SLS				S	J	2.50	5	102
S				S				SW				SW				SW				103
S	I	2.25	12	S				SW				LS	Z6	148.0	18	SW				104
S				S				SW				S	Z2	36.2	15	GL				105
LS				LS								I				S				106
PS				PS								SLS				S	Y	17.6	6	107
																				108
GL				GL				GL				GL				S				109
NF				NF				NF				NF				GL				110
TVG				TVG				TVG				SLS				TVG				111
S	A	0.50	8	S	B	0.65	15	S	Z2	36.2	18+	TVG				TVG				112
PS				PS																113
PS				PS																114
PS				PS																115
PS				PS				I				I				S	V	8.84	5	116
SW				SW				SW				I				LS				117
PS				PS				I				I				S	U	6.27	6	118
PS				PS				I				I				LS				119
S				S				SW				SW				GL				120
S	V	8.84	5	S				SW				SW				SW				121
I				I																122
PS				PS																123
S				S				SW				I				TVG				124
S	A−	−0.50	4	S				S	T	5.50	16	S	U	6.27	14	GL				125
S				S								TVG				TVG				126
NF				NF				SW				SW				SW				127
I				I				SLS				SLS				LS				128
PS				PS																129
S				S				SW				SW				SW				130
S				S				S	X	12.9	15	S	U	6.27	14	GL				131

* 100 g. of resin and 100 g. of solvent.

I Insoluble, resin unaffected by solvent.
SW Swelled, resin so affected by solvent.
TVG Transparent viscous gel formed.
GL Gelatinous liquid resulted.

TABLE XIX

	Congo															
	No. 1 Water-white				No. 4 Pale Bold Straw				No. 11 H.D. Amber Bold				No. 21 Selected Nubs			
	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color
89 Methyl acetone	GL				TVG				SW				TVG			
90 [illegible]	GL				TVG				SW				SW			
91 Methyl amyl acetate	SLS				SLS				TVG				SLS			
92 Methyl amyl alcohol	TVG				TVG				TVG				TVG			
93 Methyl n-amyl ketone	GL				NF				TVG				NF			
94 Methyl n-butyl ketone	PS				PS				SLS				TVG			
95 Methyl Carbitol	TVG				GL				TVG				GL			
96 Methyl Cellosolve	SLS				SLS				SLS				SLS			
97 Methyl Cellosolve acetate	TVG				TVG				TVG				TVG			
98 Methyl ethyl ketone	PS				PS				PS				SW			
99 Methyl isobutyl carbinol	NF				NF				TVG				NF			
100 Methyl isobutyl carbinol acetate									TVG							
101 Methyl isobutyl ketone	TVG				TVG				TVG				TVG			
102 Methyl propyl ketone	TVG				NF				NF				NF			
103 Methyl salicylate	SW				SW				SW				SW			
104 Nitrobenzol	SW				SW				SW				SW			
105 Octyl acetate	SW				SW				SW				SW			
106 Octyl alcohol	TVG				TVG				TVG				TVG			
107 Petrohol	PS				PS				PS				PS			
108 Petroleum naphtha					See	Special	Chart		on These		Solvents					
109 Phenol—[illegible]°C.	GL				GL				GL				GL			
110 Phenol—25°C.	GL				TVG				NF				NF			
111 Phenyl Cellosolve	TVG				TVG				TVG				TVG			
112 Propylene dichloride	SW				SW				TVG				SW			
113 Propylene glycol ethyl ether	SLS				SLS				SLS				SLS			
114 Propylene glycol isopropyl ether	SLS				SLS				SLS				SLS			
115 Propylene glycol methyl ether	SLS				SLS				SLS				SLS			
116 Shellacol	GL				TVG				SW				TVG			
117 Sodium hydroxide 10%	SW				SW				SW				SW			
118 Solox	GL				TVG				SW				TVG			
119 Synasol	GL				TVG				I				I			
120 Terpineol	GL				SW				SW				SW			
121 Tetrachlorethane	I				I				I				I			
122 Tetraethylene glycol	I				I				I				I			
123 Tetraethylene glycol ethyl ether	I				I				I				I			
124 Tetralin	GL				SW				SW				SW			
125 Toluol	SW				SW				SW				SW			
126 Trichlorethylene	TVG				TVG				TVG				TVG			
127 Tricresyl phosphate	SW				SW				SW				SW			
128 Triethylene glycol	I				I				I				I			
129 Triethylene glycol ethyl ether	SLS				SLS				SLS				SLS			
130 Turpentine	I				SW				SW				SW			
131 Xylol	I				SW				SW				SW			

* All determinations made with

S Soluble, [illegible]% of resin dissolved.
LS Largely soluble, 50–[illegible]% of resin dissolved.
PS Partly soluble, 25–50% of resin dissolved.
SLS Slightly soluble, 5–25% of resin dissolved.
NF Non-flowing gel.

*(Continued)**

Congo Ester				East India Macassar								East India Singapore								
				Bold				Nubs				Bold				Nubs				
Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	
S				I				I				I				I				89
SW				I				I				I				I				90
S				PS				PS				PS				PS				91
S				I				I				I				I				92
S	B	0.65	18+	I				I				I				I				93
S				PS				LS				PS				LS				94
SLS				I				I				I				I				95
SLS				I				I				I				I				96
SLS				I				I				I				I				97
PS				SLS				SLS				SLS				SLS				98
PS				I				I				I				I				99
				PS				PS				PS				PS				100
S	E	1.25	18+	I				I				I				I				101
				SLS				SLS				PS				PS				102
S				I				I				I				SW				103
S				I				I				I				SW				104
S	R	4.70	18+	SLS				SLS				S				S	Z1	27.0	14	105
S	Z1	27.0	18+	I				I				I				I				106
SLS				SLS				SLS				SLS				SLS				107
																				108
S				GL				GL				GL				GL				109
S				GL				GL				GL				NF				110
SLS				SLS				SLS				SLS				SLS				111
S				LS				LS				LS				LS				112
																				113
																				114
																				115
SW				I				I				I				I				116
SW				SLS				SLS				SLS				SLS				117
SW				I				I				I				I				118
SW				I				I				I				I				119
S				I				SLS				I				SW				120
S	Z3	46.3	18+	SW				SW				SW				SW				121
																				122
																				123
S				S				S	Z6	148.0	18	S				S				124
S				S				S	F	1.40	12	S				S	F	1.40	14	125
				LS				LS				LS				LS				126
SLS				I				I				I				I				127
I				SLS				SLS				SLS				SLS				128
																				129
S				LS				LS	Z3	46.3	13	S				S	Z6	148.0	14	130
S				S				S	F	1.40	11	S				S	I	2.25	11	131

* 100 g. of resin and 100 g. of solvent.

I Insoluble, resin unaffected by solvent.
SW Swelled, resin so affected by solvent.
TVG Transparent viscous gel formed.
GL Gelatinous liquid resulted.

TABLE XIX

		Elemi				Kauri								Manila WS			
						Pale No. 2				Brown No. 2							
		Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color
89	Methyl acetone	PS				S	T	5.50	12	S	T	5 50	18	S			
90	Methyl alcohol	PS				S	U	6 27	13	S	A–	–0.50	16	S	D	1.00	7
91	Methyl amyl acetate	S				SLS				SLS				PS			
92	Methyl amyl alcohol	S				S	Z	22 7	13	S	Z3	46 3	18+	S	X	12.9	6
93	Methyl n-amyl carbinol	S				S	T	5 50	15	S	X-Y	12 9-17.6	18+	S	T	5.50	7
94	Methyl n-butyl ketone	PS				S	Q	4 35	12	S				S	S	5.00	7
95	Methyl Carbitol	SLS				S	Z2	36 2	14	S	Z5	98.5	18+	S	X	12.9	8
96	Methyl Cellosolve	PS				S	Y	17.6	12	S	Z	22 7	18+	SW			
97	Methyl Cellosolve acetate	S				S	Z	22 7	12	S	Z2	36 2	18+	S	Z	22.7	8
98	Methyl ethyl ketone					SW				S				SW			
99	Methyl isobutyl carbinol	S				S	Z1	27 0	14	S	Z4	63 4	18+	S	W-X	10.70-12.9	7
100	Methyl isobutyl carbinol acetate	S															
101	Methyl isobutyl ketone	S				S	U	6.27	12	S	V-W	8.84-10 70	18+	S	P	4.00	8
102	Methyl propyl ketone					S	I-J	2 25-2 50	13	S	Q	4 35	18+	S	H-I	2.00-2.25	9
103	Methyl salicylate	LS				SLS				SW				NF			
104	Nitrobenzol	GL				GL				SW				SW			
105	Octyl acetate	PS				PS	Z3	46 3	10	SW				PS			
106	Octyl alcohol	S				LS				S	Z3	46.3	18	S	Z1-Z2	27.0-36.2	7
107	Petrohol					S	X	12 9	12	LS				LS	M	3.20	7
108	Petroleum naphtha					See Special Chart on These Solvents											
109	Phenol—60°C.	S	C	0 85	15	S				S				S			
110	Phenol—25°C.	LS	B	0 65	17	GL				S							
111	Phenyl Cellosolve	LS				LS				LS				LS			
112	Propylene dichloride	S				SW				SW				TVG			
113	Propylene glycol ethyl ether	S												SW			
114	Propylene glycol isopropyl ether	S												SW			
115	Propylene glycol methyl ether	S												SW			
116	Shellacol	PS				S	U	6.27	12	S	V	8.84	18	S	G	1.65	7
117	Sodium hydroxide 10%	I				SW				SLS				PS			
118	Solox					S	X	12.9	12	S	Z1	27.0	18	S	H	2.00	7
119	Synasol	SLS				LS				LS				S			
120	Terpineol					SLS				TVG				SLS			
121	Tetrachlorethane	PS				NF				SW				NF			
122	Tetraethylene glycol	I												I			
123	Tetraethylene glycol ethyl ether	S												SW			
124	Tetralin	S	A–	–0.50	3	SLS				SLS				I			
125	Toluol	LS	A–	–0 50	2	I				SW				I			
126	Trichlorethylene	S															
127	Tricresyl phosphate	PS				SW				SW				SW			
128	Triethylene glycol	I				SLS				SLS				LS			
129	Triethylene glycol ethyl ether	S												SW			
130	Turpentine	PS				I				I				I			
131	Xylol	LS	A–	–0.50	2	I				SW				I			

* All determinations made with

S Soluble, 90–100% of resin dissolved.
LS Largely soluble, 50–90% of resin dissolved.
PS Partly soluble, 25–50% of resin dissolved.
SLS Slightly soluble, 5–25% of resin dissolved.
NF Non-flowing gel.

*(Continued)**

Manila MA				Manila Loba																
				B				C				D				DK				
Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	
S				S				S	C	0.85	5	S				S	A–	–0.50	11	89
LS	C	0.85	12	S	C	0.85	5	S	D	1.00	7	S	B	0.65	10	LS	A–	–0.50	12	90
LS				S	X-Y	12.9–17.6	5	LS				PS				LS				91
S	W	10.70	9	S	V	8.84	7	LS				LS				S	U	6.27	11	92
S	N	3.40	11	S	U	6.27	6	S	U-V	6.27–8.84	6	S	P	4.00	6	S	K	2.75	12	93
LS				S	N-O	3.40–3.70	6	LS				LS				S	G	1.65	9	94
S	X	12.9	10	S	Y-Z	17.6–22.7	5	S	X-Y	12.9–17.6	7	S	X-Y	12.9–17.6	7	S	V	8.84	9	95
SW				LS				LS				LS				LS				96
S	U	6.27	8	S	V-W	8.84–10.70	5	S	V	8.84	6	S	U	6.27	6	S	N	3.40	11	97
S	D	1.00	8	S	D	1.00	5	S				S				S				98
S	W	10.70	12	S	Y	17.6	6	S	Y	17.6	6	S	W	10.70	8	S	U	6.27	13	99
																				100
S	P	4.00	9	S	S	5.00	5	S	P	4.00	6	S	S	5.00	6	S	I	2.25	8	101
S	G-H	1.65–2.00	11	S	G-H	1.65–2.00	6	S	G-H	1.65–2.00	6	S	G-H	1.65–2.00	8	S	E	1.25	12	102
PS				PS				GL				PS				PS				103
SW				SLS				SLS				SW				SW				104
S	V-W	8.84–10.7	9	S	V	8.84	5	S	Y	17.6	5	LS				S	T	5.50	10	105
S	Z1	27.0	9	S	Z3	46.3	5	S	Y	17.6	6	LS				S	Y	17.6	11	106
LS	N	3.40	12	LS	T	5.50	5	LS	T	5.50	6	LS	M	3.20	11	LS	H	2.00	12	107
																				108
S								S												109
								GL												110
LS				LS				LS				LS				LS				111
TVG				TVG				TVG				TVG				TVG				112
																				113
																				114
																				115
LS	G	1.65	12	S	I	2.25	5	S	I	2.25	6	S	F	1.40	10	LS	B	0.65	12	116
PS				LS				PS				PS				PS				117
LS	F	1.40	11	S	K	2.75	5	S	J	2.50	7	S	F	1.40	9	LS	B	0.65	12	118
S				S				S				S				S				119
SLS				PS				SW				SLS				SLS				120
NF				NF				SW				NF				NF				121
																				122
																				123
I				GL				GL				I				I				124
I				I				GL				I				I				125
TVG																				126
SW				SW				SW				NF				SW				127
LS				LS				LS				LS				LS				128
																				129
I				I				I				I				I				130
I				I				GL				I				I				131

100 g. of resin and 100 g. of solvent.

I Insoluble, resin unaffected by solvent.
SW Swelled, resin so affected by solvent.
TVG Transparent viscous gel formed.
GL Gelatinous liquid resulted

TABLE XIX

		Manila Loba (*Continued*)								Manila							
		CNE				Dust				CBB				DBB			
		Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color
89	Methyl acetone	S	A	0.50	8	S	A–	–0.50	12	S	C	0.85	6	S	A–	–0.50	9
90	Methyl alcohol	LS	A	0.50	9	LS	A–	–0.50	15	S	B	0.65	7	S	A	0.50	9
91	Methyl amyl acetate	S	Z2	36.2	10	LS				LS				PS			
92	Methyl amyl alcohol	S	X–Y	12.9–17.6	7	S	P	4.00	15	S	W	10.70	7	S	X–Y	12.9–17.6	9
93	Methyl *n*-amyl ketone	S	M	3.20	9	S	D	1.00	15	S	Q	4.35	7	S	T	5.50	8
94	Methyl *n*-butyl ketone	PS				S	C	0.85	14	S	P	4.00	8	LS			
95	Methyl Carbitol	S	V	8.84	9	S	M	3.20	13	S	W–X	10.70–12.9	9	S	W	10.70	9
96	Methyl Cellosolve	LS				LS				S	N	3.40	8	S	X	12.9	8
97	Methyl Cellosolve acetate	S	U	6.27	8	S	F	1.40	12	S	V	8.84	8	S	U–V	6.27–8.84	9
98	Methyl ethyl ketone	S				S				S				S			
99	Methyl isobutyl carbinol	S				S	Y	17.6	6	S	X	12.9	6	S	W	10.70	8
100	Methyl isobutyl carbinol acetate																
101	Methyl isobutyl ketone	S	K	2.75	7	S	A–	–0.50	12	S	J	2.50	7	S	R	4.70	8
102	Methyl propyl ketone	S	D–E	1.00–1.25	11	S	A–	–0.50	15	S	F	1.40	7	S	I	2.25	9
103	Methyl salicylate	PS				PS				SW				GL			
104	Nitrobenzol	SW				SLS				PS				SLS			
105	Octyl acetate	S	W	10.70	8	S	I	2.25	12	S	V	8.84	7	S	U	6.27	7
106	Octyl alcohol	S	X–Y	12.9–17.6	8	S	W	10.70	15	LS				S	Z2	36.2	8
107	Petrohol	LS	M	3.20	9	LS	A	0.50	18+	LS	O	3.70	8	S	L	3.00	9
108	Petroleum naphtha					See Special Chart on These Solvents											
109	Phenol—60°C.									S				S			
110	Phenol—25°C.									S				S			
111	Phenyl Cellosolve	LS				LS				LS				LS			
112	Propylene dichloride	SW								TVG				SW			
113	Propylene glycol ethyl ether																
114	Propylene glycol isopropyl ether																
115	Propylene glycol methyl ether																
116	Shellacol	LS	F	1.40	9	LS	A–	–0.50	15	S	I	2.25	8	S	E	1.25	9
117	Sodium hydroxide 10%	PS				PS				PS				PS			
118	Solox	LS	G	1.65	9	LS	A–	–0.50	15	S	H	2.00	8	S	D	1.00	10
119	Synasol	S				S				S				S			
120	Terpineol	SLS								SLS				GL			
121	Tetrachloroethane	NF				SW				SW				SW			
122	Tetraethylene glycol																
123	Tetraethylene glycol ethyl ether																
124	Tetralin	PS				PS				GL				SLS			
125	Toluol	I				I				GL				SW			
126	Trichlorethylene																
127	Tricresyl phosphate	NF				TVG				SW				SW			
128	Triethylene glycol	LS				LS				LS				LS			
129	Triethylene glycol ethyl ether																
130	Turpentine	I				I				SW				I			
131	Xylol	I				I				SW				SW			

* All determinations made with

S Soluble, 90–100% of resin dissolved.
LS Largely soluble, 50–90% of resin dissolved.
PS Partly soluble, 25–50% of resin dissolved.
SLS Slightly soluble, 5–25% of resin dissolved

*(Continued)**

Mastic				Philippine Manila Bold Pale Chips				Pontianak Bold Scraped				Sandarac				Singapore Damar No. 1				
Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	
S	A−	−0.50	7	S	A	0.50	8	S	Y	8.84	5	S	B	1.65	7	LS				89
S	A−	−0.50	7	S	A−	−0.50	11	S	J	2.50	9	PS				I				90
S				S	Z4	63.4	7	SLS				GL				LS				91
S				S	X	12.9	7	LS				S				LS				92
S				S	T	5.50	7	S	X	12.9	8	S				PS				93
S	A−	−0.50	7	S	I	2.25	9	S				S	Q	4.35	9	PS				94
S				S	X	12.9	8	S	Z4-Z5	63.4-98.5	7	GL				PS				95
S				S	U	6.27	3	S	X	12.9	8	S				PS				96
S				S	Y	17.6	3	S	Z1	27.0	8	S				SLS				97
NF				SW				S				SW				PS	A−	−0.50	WC	98
S				S	X	12.9	7	S	Z	22.7	6	S				LS				99
S												GL				LS				100
S				S	P	4.00	7	S	V-W	8.84-10.70	5	S				PS				101
S	A−	−0.50	5	S	G-H	1.65-2.00	7	S	U-V	6.27-8.84	5	S	J	2.50	8	LS	A−	−0.50	WC	102
LS	C	0.85	7+	SW				SW				SLS				S	G	1.65	2	103
LS	A	0.50	9	SW				SW				GL				SW				104
S	A−	−0.50	6	LS	Z5	98.5	10	SW				LS				S				105
S	M	3.20	6	S	Z2	36.2	6	LS				LS				LS				106
S	O	3.70	5	S	L	3.00	10	S	X	12.9	9	S	E	1.25	7	PS				107
																				108
				S				S								GL				109
LS	M	3.20	17	GL				GL				SW				NF				110
S				LS				LS				TVG				PS				111
S				SW				SW				TVG				S				112
S												S				PS				113
S												S				PS				114
S												S				PS				115
S	A−	−0.50	7	S	C	0.85	10	S	U-V	6.27-8.84	9	S	F	1.40	7	PS				116
SW				GL				GL				SW				SW				117
LS				S	C	0.85	11	S	R	4.70	9	S				PS				118
S				S				S				S				PS				119
PS				PS				SLS				PS				S				120
S	U	6.27	8	SW				SW				TVG				S				121
SLS												I				I				122
S												S				PS				123
LS	C-D	0.85-1.00	7	PS	Z5	98.5	18	SW				SLS				S				124
S	A−	−0.50	6	SW				I				SLS				S				125
S												TVG				S				126
LS				SW				SW				GL				NF				127
SLS				LS				LS				I				I				128
S												S				PS				129
PS				I				SW				SLS				S				130
S	A−	−0.50	6	SW				SW				SLS				S				131

100 g. of resin and 100 g. of solvent.

I Insoluble, resin unaffected by solvent.
SW Swelled, resin so affected by solvent.
TVG Transparent viscous gel formed.
GL Gelatinous liquid resulted.
NF Non-flowing gel.
WC White and cloudy

TABLE

SOLUBILITY, VISCOSITY AND COLOR OF NATURAL

(Accroides, Boea, the Congos, the Kauris, the Manilas, the Philippine Manilas and Ponti-

	Trade Name	Manufacturer	Batavia Damar A D				Batavia Damar Standard A E				Batu East India Nubs and Chips			
			Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color
1	D. C. Naphtha	Standard Oil Co. of Ohio	S	A−	0.50−	4	S	A−	0.50−	4	PS	L	3.00	12
2	Varnolene	Standard Oil Co. of Ohio	S	A	0.50	5	S	A	0.50	3	PS	V	8.84	12
3	Kerosene	Standard Oil Co. of Ohio	S	D	1.00	3	S	D	1.00	3	SLS			
4	Torch Oil	Standard Oil Co. of Ohio	S	W	10.70	7	S	V	8.84	6	SLS			
5	Solvent Naphtha 54	Standard Oil Co. of Ohio	S	A−	0.50−	4	S	A−	6.50−	4	SLS			
6	Solvent Naphtha 55	Standard Oil Co. of Ohio	S	A−	0.50−	5	S	A−	0.50−	4	SLS			
7	V. M. P. Naphtha	Standard Oil Co. of Ohio	S	A−	0.50−	4	S	A−	0.50−	4	SLS			
8	Varsol No. 2	Standard Oil Co. of Ohio	S	A	0.50	4	S	A	0.50	3	SLS			
9	Solvesso No. 1	Standard Oil Co. of N. J.	S	A−	0.50−	4	S	A−	0.50−	4	S	Z	22.7	16
10	Solvesso No. 2	Standard Oil Co. of N. J.	S	A−	0.50−	3	S	A−	0.50−	3	S	Z1	27.0	17
11	Solvesso No. 3	Standard Oil Co. of N. J.	S	B	0.65	4	S	A	0.50	3	S	Z6	148	17
12	Solvesso No. 4	Standard Oil Co. of N. J.	S	G	1.65	6	S	E	1.25	5	S	Z6	148	17
13	Petrobenzol	Anderson Prichard Oil Co.	S	A−	0.50−	4	S	A−	0.50−	3	SLS			
14	Troluoil	Anderson Prichard Oil Co.	S	A−	0.50−	4	S	A−	0.50−	4	SLS			
15	Apcothinner	Anderson Prichard Oil Co.	S	A−	0.50−	4	S	A−	0.50−	4	PS	P	4.00	12
16	Apco 125	Anderson Prichard Oil Co.	S	B	0.65	4	S	A	0.50	3	PS	U	6.27	13
17	Apco B-75	Anderson Prichard Oil Co.	S	E	1.25	4	S	C	0.85	3	SLS			
18	Sunoco Spirits	Sun Oil Co.	S	A	0.50	4	S	A	0.50	3	SLS			
19	Spec. Sunoco Spirits	Sun Oil Co.	S	A	0.50	3	S	A	0.50	3	SLS			
20	Sinclair Rubber Solvent	Sinclair Oil Co.	S	A−	0.50−	4	S	A−	0.50−	4	LS	I	2.25	11
21	Sinclair Naphthol	Sinclair Oil Co.	S	A−	0.50−	4	S	A−	0.50−	3	SLS			
22	Sinclair V.M.P. Naphtha	Sinclair Oil Co.	S	A−	0.50−	4	S	A−	0.50−	4	SLS			
23	Sinclair Solvent	Sinclair Oil Co.	S	C	0.85	4	S	A	0.50	3	SLS			
24	Sinclair Odorless Insecticide Base	Sinclair Oil Co.	S	F	1.40	3	S	D	1.00	3	SLS			
25	Shell Lacquer Diluent "A"	Shell Oil Co.	S	A−	0.50−	WC	S	A−	0.50−	WC	LS			
26	Shell Lacquer Diluent "B"	Shell Oil Co.	S	A−	0.50−	3	S	A−	0.50−	4	SW			
27	Shell Lacquer Diluent "C"	Shell Oil Co.	S	A−	0.50−	WC	S	A−	0.50−	WC	SLS			
28	Shell TS-1 Solvent	Shell Oil Co.	S	E	1.25	5	LS	B	0.65	3	GL			
29	Shell TS-11 Solvent	Shell Oil Co.	S	A−	0.50−	3	S	A−	0.50−	4	S	V	8.84	18+
30	Shell TS-16 Solvent	Shell Oil Co.	S	A−	0.50−	4	S	A−	0.50−	5	S	Y	17.6	18+
31	Shell TS-28 Solvent	Shell Oil Co.	S	A	0.50	4	S	A	0.50	5	S	Z1-Z2	27.0-36.2	18+
32	Shell Rubber Solvent "A"	Shell Oil Co.	S	B	0.65	6	LS	A−	0.50−	WC	GL			
33	Shell Odorless Kerosene	Shell Oil Co.	S	P-Q	4.00-4.35	5	LS	F	1.40	3	NF			
34	Shell P&V Thinner	Shell Oil Co.	S	D	1.00	5	LS	A	0.50	3	PS			
35	Shell Paint Base Spirits	Shell Oil Co.	S	E	1.25	5	LS	A	0.50	3	GL			
36	Shell White Spirits	Shell Oil Co.	S	F	1.40	5	LS	B	0.65	4	NF			
37	Union Solvent No. 8	Union Oil Co. of Calif.	S	A−	0.50−	4	S	A−	0.50−	4	S	Z1	27.0	18+
38	Union Solvent No. 30	Union Oil Co. of Calif.	S	A	0.50	4	S	A	0.50	5	S	Z4	63.4	18+
39	Union Solvent No. 40	Union Oil Co. of Calif.	S	B	0.65	4	S	B	0.65	5	S	Z5	98.5	18+
40	Standard Thinner No.200	Standard Oil Co. of Calif.	S	A	0.50	6	S	A−	0.50−	6	SW			
41	Standard Thinner No.250	Standard Oil Co. of Calif.	S	A	0.50	6	S	A−	0.50−	6	PS			
42	Standard Thinner No.300	Standard Oil Co. of Calif.	S	B	0.65	6	S	B-C	0.65-0.85	6	PS			
43	Standard Thinner No.350	Standard Oil Co. of Calif.	S	E	1.25	6	S	E	1.25	5	LS			
44	Socal Thinner No. 355-L	Standard Oil Co. of Calif.	S	C	0.85	6	S	B	0.65	5	S			

* All determinations made with 100

S Soluble, 90–100% of resin dissolved.
PS Partly soluble, 25–50% of resin dissolved.
I Insoluble, resin unaffected by solvent.
TVG Transparent viscous gel formed.
NF Non-flowing gel.
WC White and cloudy.

XX

RESINS IN VARIOUS PETROLEUM NAPHTHAS*

anaks Are All Insoluble in These Solvents and Are Not Indicated in the Table.)

Black East India Bold Scraped				East India Macassar Nubs				East India Singapore Nubs				Singapore Damar No. 1				Congo Ester				
Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	Solubility	Viscosity	Poises	Color	
SW				PS	C	0.85	10	PS	F	1.40	10	S				S	A	0.50	10	1
SW				LS	L	3.00	10	LS	R	4.70	11	S				S	B	0.65	11	2
SW				PS	U	6.27	10	LS	V	8.84	12	S	F	1.40	4	S	E	1.25	10	3
SW				SLS				PS	Z6	148	13	S				S	Q	4.35	10	4
SW				PS	B	0.65	9	SLS				S	A−	0.50−	WC	S	A	0.50	10	5
SW				SLS				SLS				S	A−	0.50−	WC	S	A	0.50	10	6
SW				PS	F	1.40	10	PS	H	2.00	11	S				S	A	0.50	10	7
SW				LS	O	3.70	10	LS	P	4.00	12	S	A	0.50	3	S	A	0.50	10	8
S	Q	4.35	14	LS	D	1.00	10	S	F	1.40	10	S	A−	0.50−	WC	S	A	0.50	11	9
S	W	10.70	14	LS	J	2.50	11	S	W	10.70	14	S	A−	0.50−	4	S	A	0.50	11	10
S	Z2	36.2	15	S	V	8.84	12	S	Y	17.6	14	S	C	0.85	4	S	L	3.00	12	11
S	Z5	98.5	17	S	Z	22.7	14	S	Z2	36.2	15	S	L	3.00	5	S	A	0.50	11	12
SW				PS	B	0.65	7	SLS				S	A−	0.50−	WC	S	A	0.50	9	13
SW				PS	C	0.85	8	SLS				S				S	A	0.50	10	14
SW				PS	D	1.00	9	PS	E	1.25	10	S	A−	0.50−	3	S	B	0.65	11	15
SW				PS	D	1.00	7	PS	H	2.00	11	S	C	0.85	3	S	C	0.85	10	16
SW				SLS				PS	K	2.75	11	S	A−	0.50−	3	S	C	0.85	10	17
PS	Z1	27.0	18	PS	I	2.25	10	PS	O	3.70	11	S				S	A	0.50	10	18
SW				PS	F	1.40	9	PS	J	2.50	11	S				S	A	0.50	10	19
S	W	10.70	12	PS	B	0.65	8	SLS				S	A−	0.50−	WC	S	A	0.50	10	20
S	W	10.70	12	PS	C	0.85	9	SLS				S	A−	0.50−	4	S	A	0.50	11	21
LS	Z1	27.0	13	PS	D	1.00	9	SLS				S				S	A	0.50	10	22
SW				LS	I	2.25	9	PS	I	2.25	11	S				S	B	0.65	10	23
SW				PS	I	2.25	8	PS	L	3.00	10	S	E	1.25	4	S	E	1.25	10	24
SLS				SLS				SLS				S	A−	0.50−	WC	S				25
SW				LS	L	3.00	7	LS	S	5.00	11	S	A	0.50	2	S				26
SW				SLS				SLS				S	A−	0.50−	WC	S				27
GL				SLS				LS	Z2	36.2	11	S	B	0.65	1	S				28
LS	V	8.84	CB	SLS				LS	I	2.25	11	S	A−	0.50−	2	S				29
LS	W	10.70	CB	LS	P	4.00	12	LS	X	12.9	12	S	A−	0.50−	2	S				30
LS	Y	17.6	CB	SLS				S	V	8.84	12	S	A−	0.50−	2	S				31
PS				SLS				LS	T	5.50	12	S	A	0.50	5	S				32
GL				SLS				PS				S	H	2.00	2	S				33
GL				SLS				S	Y	17.6	12	S	A	0.50	2	S				34
SLS				SLS				S	Z	22.7	12	S	A	0.50	2	S				35
SLS				SLS				LS	Z1	27.0	11	S	B	0.65	2	S				36
S	U	6.27	18+	S	G	1.65	11	S	F	1.40	13	S	A−	0.50−	3	S	E	1.25	18+	37
S	X	12.9	18+	S	M	3.20	13	S	M	3.20	13	S	A−	0.50−	4	S	L	3.00	18+	38
S	Z2	36.2	18+	S	W	10.70	13	S	W	10.70	13	S	B	0.65	4	S	U	6.27	18+	39
SW				PS				LS				S	A−	0.50−	6	SLS				40
SW				PS				LS				S	A−	0.50−	5	SLS				41
SW				LS				S	V-W	8.84–10.70	12	S	A	0.50	4	PS				42
SW				S	X-Y	12.9–17.6	11	S	X	12.9	16	S	D	1.00	4	LS				43
TVG				S	U-V	6.27–8.84	15	S	U	6.27	15	S	A	0.50	4	S	M	3.20	18+	44

g. of resin and 100 g. of solvent.

LS Largely soluble, 50–90% of resin dissolved.
SLS Slightly soluble, 5–25% of resin dissolved.
SW Swelled, resin so affected by solvent.
GL Gelatinous liquid resulted.
CB Cloudy brown.

saturated borax solution, and sodium hydroxide solutions. It swells in 10 per cent potassium hydroxide.

Accroides is insoluble in coal-tar hydrocarbons. Influence of the benzene ring on its solubility in aromatic esters is shown by its slight solubility in methyl salicylate and partial solubility in dimethyl phthalate; it is largely soluble in all the straight-chain esters used.

Solubilities in the ethers decrease as the number of carbon atoms in the alkyl radicals of the ethers increase. Although the resin is largely soluble in ethyl ether, it is only slightly soluble in isopropyl and insoluble in *n*-butyl ethers.

Hydroxyl groups have a tendency to aid the solubility of accroides in the terpenes. Terpineol is an unsaturated terpene with one hydroxyl group. The resin is largely soluble in it and is partly soluble in dipentene, slightly soluble in turpentine, and insoluble in Hercosol 80.

The influence of the complexity of the molecule on the solubility of accroides is again revealed by results obtained on the alcohol-ethers. The resin is largely soluble in Cellosolve and only partly soluble in Carbitol and butyl Carbitol.

The chlorinated compounds show feeble solvency powers for accroides. This is reflected even in dichloroethyl ether, in which the resin is only partly soluble. In normal ethyl ether, accroides is largely soluble.

Congo Solubility. Congo is the most insoluble of the natural resins in organic solvents unless thermally processed or masticated. Any attempts to prepare 50 per cent solutions by mixing with single solvents and agitating (the usual method of putting resins into solution) have always resulted in the formation of non-flowing gels, swelling of the resin, transparent viscous gels, or, at best, gelatinous liquids. Hexalin acetate has been suggested as a solvent for congo, but only in low resin concentrations (15 per cent). On the basis of such low resin content, a number of solvents can claim solvency for Congo resins.

On long standing, congo will dissolve in a number of solvent combinations. This fact was discovered after mixtures of equal parts of congo No. 4 and solvent had been standing for about six months. Almost complete solubility was observed with solvents composed of equal mixtures of methanol-isopropanol, methyl acetone-isopropanol, and methyl propyl ketone-isopropanol. Over the same period of time, 1 part of congo No. 4 and 2 parts of the last-named solvent combination formed a complete solution. Alcohols, esters, and ketones attack the resin best and numerous solvent combinations using these can be formed which will dissolve congo.

The following solubility experiments were performed on congo No. 2 and No. 4. The data obtained for each are given separately. The resin and solvent were agitated overnight on an end-over-end mixing machine. In the numerous cases where complete solubility was not obtained, continued agitation for an additional 24 hours did not alter the results.

Congo No. 2

(*a*) Fresh sample, roughly ground immediately before use.

25 g. resin
50 g. isopropanol
50 g. methyl propyl ketone

Results: Resin largely soluble; solution cloudy; gelatinous particles visible.

(*b*) Same as (*a*) except that the resin had been in a ground condition several months.

Results: Resin more soluble than in case (*a*); solution clearer, a small amount of gelatinous particles still visible.

(*c*) Powdered sample used which had been kept in this condition for 5 to 6 months.

25 g. resin
100 g. isopropanol

Results: Resin completely soluble with no visible gelatinous particles; solution clear.

Congo No. 4

Freshly powdered resin used.

TABLE XXI

Weight of Resin	Weight of Solvent	Results
25 g.	100 g. Butyl acetate	Partly soluble
25 g.	50 g. Isopropanol 50 g. Methyl propyl ketone	
25 g.	100 g. Ethyl acetate	Evenly dispersed but not completely soluble
25 g.	100 g. Isopropanol	
25 g.	100 g. Ethyl alcohol	
25 g.	50 g. Ethyl acetate 50 g. Butyl acetate	
25 g.	100 g. Methyl propyl ketone	Partly soluble

The solutions attempted with congos No. 2 and No. 4 were of low resin contents (20 per cent). With one exception, complete solubility was not obtained and indications were that much longer time periods were needed. Exposure of the resin to the atmosphere appears to increase the solubility of Congo resins. This can be concluded from the

progressive increase in solubility in those congo No. 2 samples which were kept in a ground or powdered condition for varying lengths of time. The conclusion is apparently confirmed by the ready solubility of congo dust. (This grade is actually the original exposed surface layers of the better grades and is a by-product of their cleaning.)

Fifty per cent congo dust solutions have been prepared in a number of solvents merely by agitating the mixture overnight. (Table XXII.)

TABLE XXII

Solvent	Viscosity of Solution (Gardner-Holdt)	Color of Solution (Gardner)
Ethanol	F	15
Isopropanol	N	15
Butanol	P	15
Ethyl acetate	C	15
Butyl acetate	M	15
Amyl acetate	P	15
Methyl propyl ketone	E	15

Such solutions after being clarified by filtration have been used as spirit varnishes, traffic paint vehicles, sanding sealers, and in lacquer formulation.

The use of raw congo in lacquers has not been extensively investigated by the authors. It is compatible with ethyl cellulose and gives a clear, hard, glossy lacquer film. With nitrocellulose, a blushed film was obtained, but this was considered to be due to the lack of a proper solvent balance rather than to outright incompatibility. It appears to be definitely incompatible with cellulose acetate.

Grinding methods have been resorted to in an attempt to attain faster solution rates. The gels formed when congo is mixed with certain solvents can be considerably reduced in viscosity by passage through a colloid mill. In connection with grinding the use of a pebble mill has also been investigated. Because of the tendency of the gel to bind the pebbles together, satisfactory grinding action cannot be secured when equal parts of resin and solvent are used. In a test run, 1 part of congo and 2 parts of isopropanol were placed in a pebble mill and rotated for several days. At intervals, samples of equal volume were withdrawn and placed in stoppered bottles to permit settling of insoluble matter. It was noticed that as the grinding progressed, less and less gelatinous matter settled out, indicating the gradual solution of the resin.

In another experiment, a solution of congo No. 2 was prepared by first powdering the resin in a ball mill. An equal weight of isopropanol

and an equal weight of methyl propyl ketone was added and grinding continued for 24 hours. After this period, the mixture was bottled and, after standing for 2 weeks, complete solution of the resin was observed.

As the results of the preceding experiments indicated the possibility of congo containing a soluble portion which acts as an adhesive (binding the insoluble constituents together with the formation of gel-like masses), the authors made a short study of the solubility of Congo resin acids.

The separation was performed by mixing 1 part of congo No. 11 and 2 parts of water together with an excess of sodium hydroxide (as calculated from the acid number of the resin). After agitating for several hours, the mixture was centrifuged and the solution of the resin acids in the form of sodium salts poured off from the insoluble matter. By acidifying with hydrochloric acid, the resin acids were precipitated. After filtering, washing, and air-drying, they were obtained in a dry, solid state. The resin acids were found to be completely and easily spirit soluble. A method of processing congo is suggested by these results. It would involve separation of the congo into a spirit-soluble portion, which may be used in lacquers, spirit varnishes, paper coatings, etc., and an insoluble portion which, after thermal processing, can be used in oil varnishes.

After thermal processing, congo is soluble in a wide range of solvents and compatible with drying oils. These solvents include the petroleum naphthas of the simple and hydrogenated types, the varnolenes, the coal-tar naphthas, alcohols such as the butanols, and esters such as butyl acetate, terpenic solvents, ketones, ethers, the fatty acids, and the vegetable oils.

Batavia and Singapore Damars. Batavia and Singapore damars have the common property of being soluble in chlorinated compounds, coal-tar hydrocarbons, petroleum hydrocarbons, terpenes, and tetralin. Batavia damar is also soluble in esters (amyl acetate, butyl butyrate, butyl propionate, methyl salicylate, and octyl acetate), ethers (butyl, ethyl, and isopropyl), carbon disulfide, and paraffinic, naphthenic, and hydrogenated petroleum solvents. The resin is soluble in esters of higher molecular weight. The higher alcohols, i.e., isopropyl, *n*-butyl and *sec*-amyl, have greater solvent action on it than the lower ones. The damars show some solubility in alcohols of higher molecular weight. They are partly soluble in all other alcohols except the polyhydric alcohols (diethylene, triethylene, and tetraethylene glycols) in which they are insoluble, and benzyl alcohol in which they are largely soluble.

Batavia damar is largely soluble in acetone, methyl acetone, butyl Carbitol, dioxane, and linoleic acid. It is partly soluble in isopropyl acetate, acetone, all alcohol ethers except butyl Carbitol, diethylene glycol monoacetate, Cellosolve acetate, acetic acid, ethylene glycol diethyl ether, ethylene oxide, diethylene oxide, propylene oxide, and glycol ether acetate. It swells in dimethyl phthalate, ethyl abietate, aniline, hexalin, nitrobenzene and tricresyl phosphate. It is insoluble in glycol monoacetate and glycol diacetate. With phenol at 60°C. it gives a gelatinous liquid; at 25°C. it forms a non-flowing gel.

Singapore damar is only partly soluble in the alcohols in which it was tested. It is soluble in amyl acetate, methyl salicylate, octyl acetate, and ethyl and isopropyl ethers. It is largely soluble in butyl butyrate, butyl Carbitol, dioxane, and linoleic acid, and partly soluble in diethyl carbonate, ethyl acetate, isopropyl acetate, dichlorethyl ether, acetone, alcohol-ethers except Carbitol, Cellosolve acetate, acetic acid, ethylene glycol diethyl ether, and ethylene oxide. It swells in dimethyl phthalate and ethyl abietate, and gives a gelatinous liquid in phenol.

East Indias. Batu nubs and chips, black east india, pale east india Macassar, and pale east india Singapore are insoluble in most alcohols. Batu and black east india swell in benzyl alcohol and are partly soluble in denatured alcohols. Pale east india Macassar is soluble and forms a cloudy solution in isopropyl alcohol; pale east india Singapore is partly soluble in the same alcohol. Singapore nubs swell in benzyl alcohol. In general, the east indias are soluble in chlorinated compounds. Batu and black east india swell in carbon tetrachloride; macassar nubs form a gelatinous liquid and singapore nubs a transparent viscous gel with carbon tetrachloride. Amyl chloride gives similar results.

All the East India resins are soluble in the coal-tar hydrocarbons; cloudy solutions may result with benzene and toluol. The only ester in which any of the east indias is soluble is octyl acetate which dissolves black east india and pale east india Singapore; diethyl carbonate dissolves pale east india Macassar nubs. The east indias are soluble in butyl ether. Macassar gives cloudy solutions in isopropyl ether.

In contrast to the damars, to which the east indias are related, the East India resins do not show ready solubility in petroleum solvents. Batu is only slightly or partially soluble in paraffin or naphthenic hydrocarbons or mixtures of the two. Ready solubility is obtained in hydrogenated petroleum solvents or in mixtures of petroleum and coal-tar hydrocarbons. Black east india only swells in the usual variety of

mineral spirits, and shows the same effect in paraffinic, naphthenic, or combination petroleum hydrocarbons. The resin is soluble in hydrogenated petroleum solvents as well as mixtures of coal-tar and petroleum hydrocarbons.

The pale east indias show considerable variation in solubility in petroleum solvents of the paraffinic type as well as the naphthenic or mixture types. In the range of commercial solvents tested, only the hydrogenated petroleum solvents completely dissolve the east indias. Commonly, the addition of coal-tar solvents markedly aids solution.

Elemi. Elemi is soluble or largely soluble in *sec*-amyl, benzyl, and *n*-butyl alcohols, chlorobenzene and chloroform, coal-tar hydrocarbons, amyl acetate, butyl acetate, butyl butyrate, butyl propionate, ethyl abietate, isopropyl acetate, ethyl ether, Hercosol 80, terpineol, the alcohol-ethers, glycol monoacetate, carbon disulfide, ethylene glycol diethyl ether, ethylene oxide, glycol diacetate, hexalin, phenol, propylene oxide, and tetralin.

It is partly or slightly soluble in denatured alcohol, diacetone, and isopropyl and methyl alcohols, chlorinated compounds other than chlorobenzene and chloroform, butyl lactate, dimethyl phthalate, ethyl acetate, methyl salicylate, octyl acetate, ethers other than those given above, ketones, dipentene, turpentine, diethylene glycol monoacetate, Cellosolve acetate, acetic acid, glycol ether acetate, tricresyl phosphate, paraffin, and hydrogenated petroleum solvents.

Kauri. Pale and brown kauris are soluble in all the alcohols tested except that the brown swells in benzyl alcohol. These alcohols include *sec*-amyl, Ansol, benzyl, *n*-butyl, diacetone, isopropyl, Shellacol, methyl, and Solox. The kauris are also soluble in amyl, butyl, and ethyl acetate, acetone and methyl acetone, Cellosolve, butyl Carbitol, dioxane, and phenol. In addition, the pale grade is soluble in tetralin, aniline, and chlorobenzene which only swell or gel the brown.

Both the pale and the brown varieties are insoluble or gelled in amyl chloride, carbon tetrachloride, coal-tar hydrocarbons, diethyl carbonate, dimethyl phthalate, ethyl abietate, methyl salicylate, butyl and dichloroethyl ethers, and terpenic compounds. Pale kauri is partly soluble in Hercosol 80 and slightly soluble in terpineol, hexalin, nitrobenzene, and tricresyl phosphate. The kauris are insoluble in the paraffinic, hydrogenated, and naphthenic petroleum solvents.

Manilas. Petroleum distillates, whether paraffinic or naphthenic in base and whether low or high boiling, have no effect on these resins. Hydrogenated petroleum solvents may sometimes attack the resin enough to swell the particles but have no further effect.

Coal-tar solvents, such as benzol, toluol, and xylol, may swell the particles or even form rubbery gelatinous masses with Manila resins.

Turpentine and dipentene either swell the particles slightly or do not attack them at all. The other terpenic solvents, Hercosol 80 and terpineol, formed gelatinous masses and in some cases dissolved the resins.

Chlorinated solvents (carbon tetrachloride, amyl chloride, monochlorobenzene, and tetrachloroethane) either swelled the particles or formed gelatinous masses.

Manila loba C, Philippine manila bold pale chips, pontianak bold scraped, and boea hard bold amber form gelatinous liquids, swell, or are insoluble in coal-tar hydrocarbons. The influence of the benzene ring in decreasing their solubility in other solvents is apparent in the cases of benzyl alcohol, chlorobenzene, dimethyl phthalate, methyl salicylate, and nitrobenzene, inasmuch as the solubility decreases when compared with other solvents of the same type. This behavior is most noticeable in the alcohols. It does not hold for solutions in aniline and phenol.

In the chlorinated aliphatic hydrocarbons, solubility of the resin increases with the number of chlorine atoms in the molecule. Amyl chloride swells the resin; it is largely soluble in ethylene dichloride and is soluble in acetylene tetrachloride.

The alcohols tried were: methyl, three anhydrous denatured ethyl alcohol formulae, isopropyl, *n*-butyl, *sec*-amyl, diacetone, and benzyl alcohols. The boea was largely, but not completely, dissolved by all except the benzyl alcohol, with which it formed a gelatinous mass. The remaining Manila resins were completely soluble in all the alcohols, except that one sample of loba was only swelled by benzyl alcohol and a sample of CBB formed a gelatinous mass with the same solvent. The viscosity of these solutions showed a marked increase with each increase in the length of the chain in the aliphatic alcohols. The benzyl alcohol solutions were the most viscous of all, and the pontianak solutions were much more viscous than the corresponding solutions of the half-hard Manila resins.

Philippine manila and pontianak are soluble in amyl and butyl acetates, which form gelatinous liquids with loba C. Loba C and pontianak are soluble and Philippine manila is largely soluble in butyl lactate. Loba is soluble in octyl acetate, in which Philippine manila is only slightly soluble and pontianak swells.

The alcohol-ethers, Cellosolve and butyl Carbitol, gave viscous solutions.

Ethyl acetate completely dissolved all the samples. Butyl, amyl,

and octyl acetates and butyl lactate dissolved some samples and swelled or formed gelatinous masses with the remainder. Diethyl carbonate, methyl salicylate, dimethyl phthalate, and methyl abietate swelled or formed gelatinous masses with the resins.

Dioxane, aniline, hexalin, and tetralin completely dissolved some samples and partly dissolved or formed gelatinous masses with the remainder. Nitrobenzene and tricresyl phosphate swelled these resins. All the Manila resins were soluble in phenol at 60°C.

Loba, Philippine manila, and pontianak are soluble or largely so in ethyl ether, acetone, methyl acetone, butyl Carbitol, Cellosolve acetate, aniline, and phenol at 60°C. In addition, Philippine manila and pontianak are soluble in dioxane.

Boea was largely but not completely dissolved by acetone and methyl acetone. It was completely dissolved in phenol at 60°C. It swelled or formed gelatinous masses with all the other solvents tried. The effect of the more fossilized character of boea is readily seen in this reduced solubility.

The other Manila resins, except pontianak, give solutions of low viscosity with acetone and methyl acetone. Pontianak also is dissolved, but its solutions are much more viscous. Ethyl ether gives similar results. *n*-Butyl ether either swells or does not attack the resins. Dichloroethyl ether only swells the particles.

An investigation of the use of petroleum solvents as diluents to reduce the cost of manila solutions has shown interesting and valuable results. It is known that in manila solutions with certain solvents such as pure methanol or special alcohol formulations, gummy or gelatinous masses and stringiness are occasionally encountered. Recent work[2] has shown at least a portion of this material to consist of a true gum which is soluble in water. The balance is a material of mucilaginous nature and of uncertain composition. The presence of this undissolved material is a disadvantage, since it tends to retard settling and reduce the actual resin yield. The authors have found that this incomplete solution can be remedied by addition of from 10 to 15 per cent of a coal-tar or petroleum hydrocarbon. With high aromatic types of petroleum thinners, as much as 75 per cent of the alcohol may be replaced by a petroleum thinner and complete solution of the manila obtained in concentrations as high as 50 per cent solids. The value of the so-called textile-spirit type of high aromatic petroleum solvents should be noted for this purpose.

In the mixed alcohol-hydrocarbon solvent of equal proportions used

[2] H. Jakobs, *Tectona*, 33, January, 1940.

for the dewaxing of damar, there exists a mutual solvent for damars and manilas. This common solvent gives the possibility of hardening damar spirit varnishes by the addition of manilas or increasing the adhesion of manila spirit varnishes by the addition of damar provided that a combination of alcohol-petroleum hydrocarbon or alcohol–coal tar hydrocarbon is employed.

Mastic. Mastic is soluble in benzyl, *n*-butyl, diacetone, ethyl, isopropyl, methyl, and denatured ethyl alcohols; in the chlorinated compounds acetylene tetrachloride, amyl chloride, chlorobenzene, and ethylene dichloride; in the coal-tar hydrocarbons; in the esters amyl acetate, butyl acetate, butyl butyrate, butyl propionate, diethyl carbonate, ethyl acetate, isopropyl acetate, and octyl acetate; and in ethyl and dichloroethyl ethers, methyl acetone, alcohol-ethers, Cellosolve acetate, aniline, dioxane, ethylene, glycol diethyl ether, ethylene oxide, glycol diacetate, glycol ether acetate, and propylene oxide. It is largely soluble in *sec*-amyl, denatured 5, and Solox alcohols; in butyl lactate and methyl salicylate; in butyl and isopropyl ethers; in dipentene and Hercosol 80; in butyl Carbitol, nitrobenzene, phenol, and tetralin.

Mastic is partly or only slightly soluble in diethylene, triethylene, and tetraethylene glycols; in carbon tetrachloride and chloroform; in dimethyl phthalate, ethyl abietate, acetone, terpineol, turpentine, alcohol-esters, acetic acid, carbon disulfide, and hexalin. It dissolves in the hydrogenated petroleum solvents but is only partly soluble in those of the paraffinic and naphthenic type. Noticeable is the fact that the resin is not completely insoluble in any of the solvents used.

Sandarac. Sandarac is soluble or largely soluble in the *sec*-amyl, benzyl, *n*-butyl, denatured 5, diacetone, ethyl, isopropyl, and denatured ethyl alcohols. It is no more than partly soluble in chlorinated compounds and coal-tar hydrocarbons but dissolves in amyl acetate, ethyl acetate, and isopropyl acetate, in acetone and methyl acetone ketones, and in alcohol-ethers, Cellosolve acetate, aniline, dioxane, ethylene oxide, and propylene oxide.

The ethers and terpenes have not much solvent action on the resin. Sandarac is insoluble or only partly soluble in butyl acetate, butyl butyrate, methyl salicylate, alcohol-esters, acetic acid, carbon disulfide, ethylene glycol diethyl ether, glycol diacetate, glycol ether acetate, hexalin, and tetralin. It swells or forms a gel in dimethyl phthalate, ethyl abietate, nitrobenzene, phenol, and tricresyl phosphate. Paraffinic, naphthenic, and hydrogenated petroleum solvents do not dissolve sandarac.

Viscosities of Damar Solutions. Because coal-tar solvents, petroleum solvents, and hydrogenated petroleum solvents are widely used and available, and since they are solvents for damar, a study of the viscosities of damar solutions in these solvents was made.[3]

Toluol, solvent naphtha 55, and Solvesso No. 1 were selected as respectively representative solvents of each of the three types mentioned. Their properties are listed in Table XXIII.

TABLE XXIII

Trade Name	Type of Solvent	Sp. Gr.	Distillation Range			
			Initial		Final	
			°C.	°F.	°C.	°F.
Toluol	Aromatic	0.866	109	228	111	232
Solvent naphtha 55	Paraffin	0.735	93	200	135	275
Solvesso No. 1	High aryl content petroleum	0.795	92	198	141	285

Solutions containing 10, 20, 30, 40, 50, 60, 65, and 70 per cent of damar by weight were prepared from each of the nine grades of Batavia damar in each of the three selected solvents. The damar was ground and the solvent added to it in a flask. In the 65 and 70 per cent concentrations in toluol as well as 60, 65, and 70 per cent in Solvesso No. 1, and in all solvent naphtha solutions, gentle refluxing was necessary to attain complete solution.

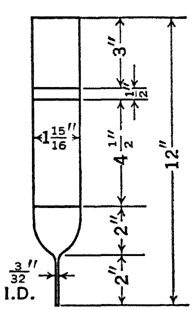


FIG. 21. Pipet viscosimeter.

The solutions were allowed to stand until all or nearly all of the dirt present had settled out, and the viscosities of the supernatant liquids determined at 25°C. Where possible, the viscosities were determined by means of the Gardner-Holdt bubble viscosimeter. However, at concentrations of 50 per cent or less, the viscosities were less than that of the lowest viscosity tube in the

[3] C. L. Mantell and A. Skett, *Ind. Eng. Chem.*, **30**, 417 (1938).

TABLE

VISCOSITIES OF

Resin Content	Damar A Reading*	Damar A Viscosity	Damar B Reading	Damar B Viscosity	Damar C Reading	Damar C Viscosity	Damar D Reading	Damar D Viscosity	Damar E Reading	Damar E Viscosity
%	Sec.	Centipoises	Sec.	Centipoises	Sec.	Centipoises	Sec.	Centipoises	Sec.	Centipoises
									Solutions in	
10	24.5	0.75	24.8	0.84	25.0	0.88	24.8	0.84	24.8	0.84
20	27.4	1.39	27.5	1.37	27.5	1.37	27.4	1.35	27.5	1.37
30	33.0	2.46	33.2	2.50	33.2	2.50	32.8	2.42	32.5	2.37
40	46.3	5.35	51.2	6 30	50.4	6.20	49.0	5.95	47.5	5.58
50	116.5	19.8	118.5	20 2	117.0	19.9	46.5	19.9	108	18.1
60	C+	90	D	100	C	85	C−	80	A	50
65	F	140	F	140	H	200	G	165	H−I	210
70	P	400	P	400	T	550	U−	610	U+	650
80	>Z6	...	...	...	>Z6	...	...	...	...	...
									Solutions in	
10	24.8	0.85	25.0	0.88	25.0	0.88	25.0	0.88	25.0	0.88
20	27.6	1.42	27.8	1.44	29.0	1.67	28.0	1.48	27.8	1.44
30	33.4	2.54	34.7	2.8	32.2	2.31	35.4	2.94	33.4	2.54
40	50.0	6.1	54.6	7.0	52.5	6.6	58.5	7.8	52.0	6.5
50	125	21.6	137	24.1	123.5	21.3	196.5	36.4	132.9	23.3
60	C−D	93	D	100	C	85	G	165	E	125
65	L−	290	K	275	I−J	238	Q	435	M	320
70	X	1290	X−Y	1525	X	1290	Y−Z	2015	X	1290
									Solutions in Solvent	
10	25.7	1.02	25.8	1.04	26.0	1.08	25.5	0.98	25.0	0.88
20	28.8	1.83	30.0	1.87	30.5	1.97	29.0	1.67	29.0	1.67
30	36.2	3.2	36.6	3.3	41.7	4.3	39.7	3.9	36.3	3.2
40	66.4	9.5	67.4	9.7	83.1	13.0	82.5	12.9	77.0	11.7
50	225.8	42.5	224	42.1	284.8	54.7	319	61.7	255.2	48.5
60	H−	190	H	200	J	250	K+	285	I	225
65	T	550	U	627	V	884	V−	850	U−V	755
70	Z	2270	Z1	2700	Z1	2700	Z2	3620	Y−Z	2015

* Readings in seconds are pipet readings; letters are Gardner-Holdt standards. Data taken at 25°C.

† These averages were calculated from the curves.

‡ This value was not included in average.

Gardner-Holdt scale and were determined by measuring the rate of flow through the orifice of a previously calibrated pipet (Fig. 21) surrounded by a water bath for purposes of temperature regulation. The results of the viscosity determinations are given in Table XXIV.

The viscosities in centipoises were plotted against concentrations for each grade of damar and for each solvent. Figures 22, 23, and 24 show these concentration-viscosity relations for the damar solutions in toluol, Solvesso 1, and solvent naphtha 55, respectively. The viscosities bear a logarithmic relation to the concentrations.

From viscosity readings taken at the previously mentioned concentrations on each curve, an average curve for all Batavia damars was plotted for each of the three solvents. The average viscosities for each

XXIV

DAMAR SOLUTIONS

Damar F Reading-ing Sec.	Damar F Vis-cosity Centi-poises	Damar Dust Read-ing Sec.	Damar Dust Vis-cosity Centi-poises	Damar A/D Read-ing Sec.	Damar A/D Vis-cosity Centi-poises	Damar A/E Read-ing Sec.	Damar A/E Vis-cosity Centi-poises	Av. Vis-cosity† Centi-poises	Av. Deviation %
Toluol									
24.7	0.82	24.8	0.84	24.8	0.84	24.5	0.75	0.83	4.1
27.8	1.43	27.5	1.37	27.5	1.37	27.0	1.28	1.32	3.7
33.5	2.58	34.0	2.66	33.0	2.46	32.8	2.42	2.52	4.0
50.5	6.20	50.5	6.20	48.4	5.80	46.5	5.40	6.10	3.6
118	20.1	120	20.6	108	18.1	98	16.1	18.0	12.5
C	85	C+	90	B	65	B	65	76.4	10.1
J–K	260	J–K	260	G–H	180	G–H	180	200	14.8
X	1290	X	1290	V	884	V	884	744	35.8
...	...	...	...	...	...	...	...	...	...
Solvesso 1									
24.6	0.81	25.0	0.88	25.5	0.98	25.0	0.88	0.88	3.3
28.3	1.54	28.3	1.54	30.2	1.92	29.0	1.67	1.48	3.0
35.5	2.95	35.4	2.94	36.7	3.30	34.8	2.82	2.91	8.1
60.4	8.2	62.5	8.6	55.1	7.1	52.2	6.5	7.21	9.7
184	33.9	199.4	37.1	139.9	24.7	126.6	22.0	23.4	13.5
F+	145	F+	145	C–D	93	C	85	119	18.8
R	470	V	884	P	400	L–	290	351	21.2
Y–Z	2015	Z2–	3600	Y	1760	X	1290	1727	21.9
Naphtha 55									
25.0	0.88	25.0	0.88	25.5	0.98	25.4	0.96	0.97	6.11
28.2	1.52	28.9	1.66	29.0	1.67	29.0	1.67	1.70	5.09
34.8	2.9	33.9	2.7	39.2	3.8	37.0	3.4	3.71	9.87
65.9	9.4	71.1	10.4	73.5	10.9	65.3	9.2	10.8	9.90
542	108.2	226.5	42.6	215	40.3	209.0	39.1	42.3	10.3
L	300	L–	290	I	225	D	100	241	19.7
X	1290	W	1070	U–V	755	T	550	809	26.4
Z6+‡	>14800	Z2	3620	Z1	2700	Y	1760	2760	18.7

concentration are included with the data in Table XXIV. The average viscosity curve for each solvent is shown in Fig. 25.

To assay the usefulness of these average curves, the per cent average deviation at each concentration was obtained by first taking readings of viscosities from the curves at the different concentrations and then calculating the per cent difference between each reading and the average viscosity for that concentration. The resulting per cent deviations were averaged to give the per cent average deviations, shown in the last column of Table XXIV.

The results of this investigation may be summarized as follows:

1. The more powerful solvents tend to yield slightly lower viscosities.

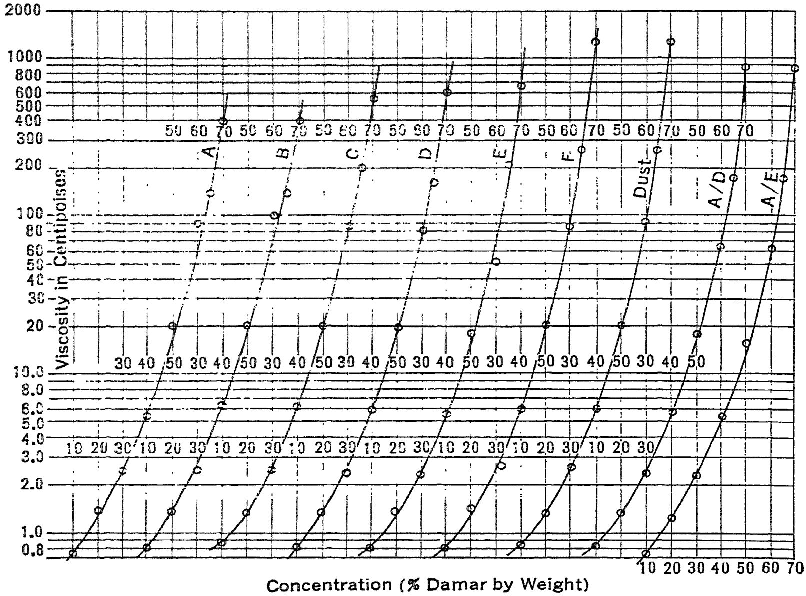


FIG. 22. Concentration-viscosity relations of solutions of Batavia damars in toluol.

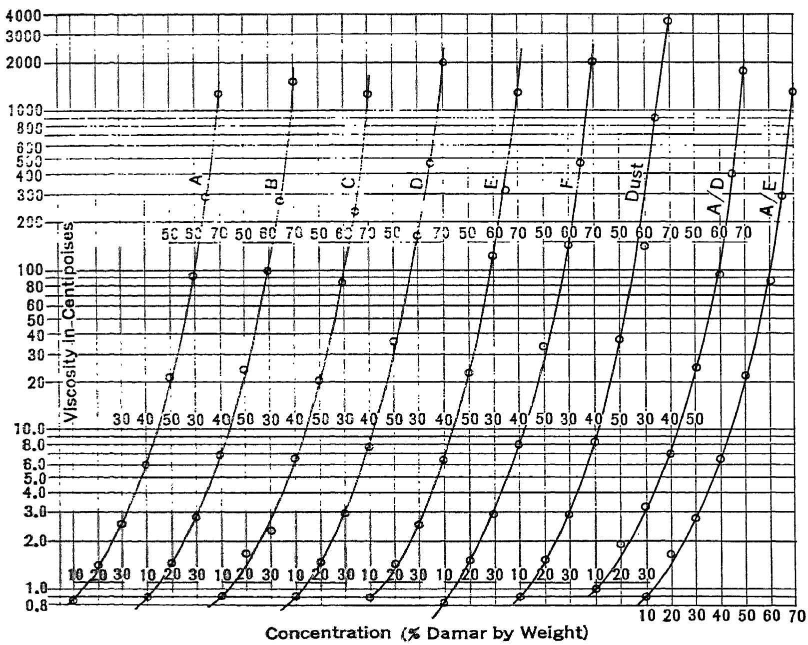


FIG. 23. Concentration-viscosity relations of solutions of Batavia damars in Solvesso 1.

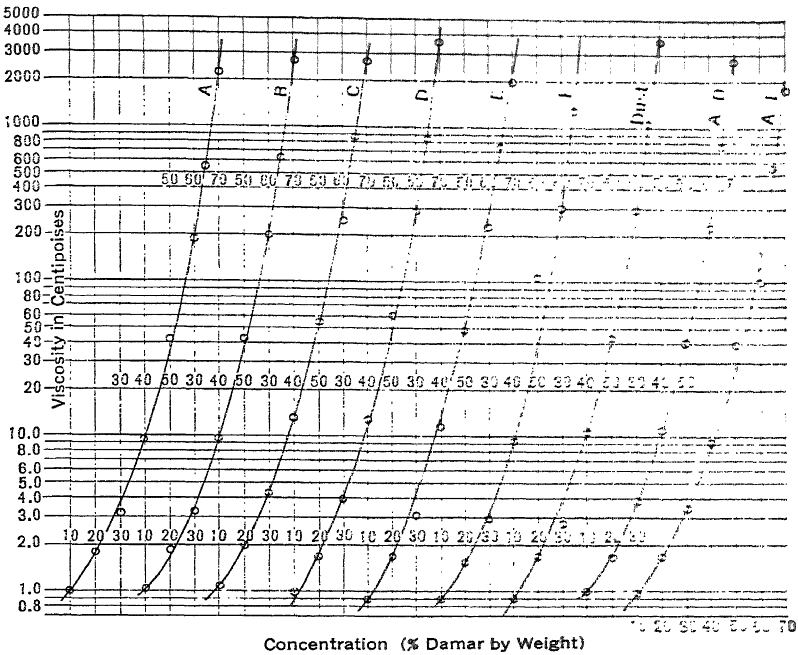


FIG. 24. Concentration-viscosity relations of solutions of Batavia damars in solvent naphtha 55.

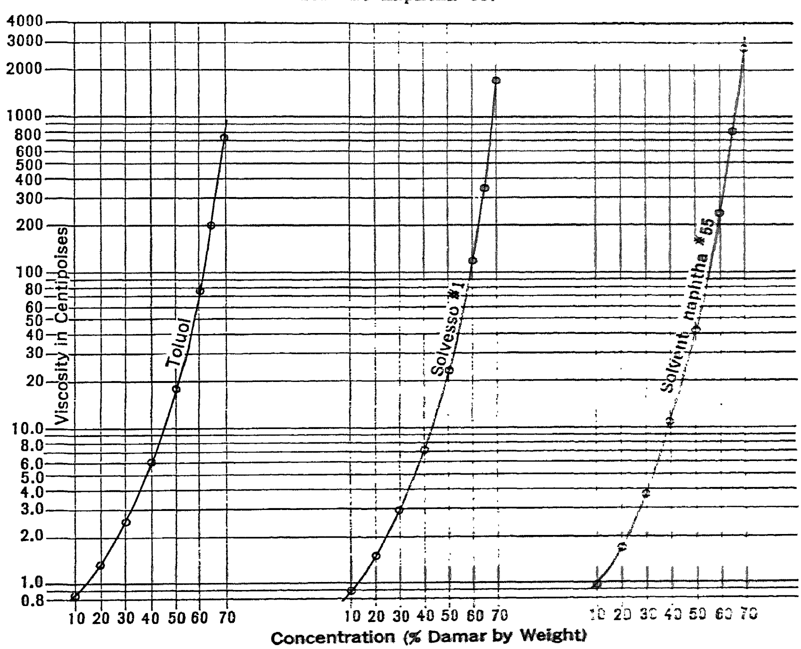


FIG. 25. Relation of concentration to average viscosity for Batavia damar solu-

2. The distillation ranges of petroleum solvents and hydrogenated petroleum solvents have an effect on the viscosities of Batavia damar solutions; the solvents with higher distillation ranges give Batavia damar solutions of higher viscosities.

3. The viscosities of Batavia damar solutions increase logarithmically with increase in concentration.

4. Toluol is the best solvent of the three for damar, with Solvesso No. 1 second, and solvent naphtha 55 third, as illustrated by the lower viscosities of the toluol curve and by the differences in the slopes of the three curves in Fig. 25.

5. Batavia damars F and dust increase in viscosity enormously after the 50 per cent concentration point is reached.

6. The curves may be used to determine the concentration of solution necessary to obtain a desired viscosity, or to determine the concentration of a solution by its viscosity.

7. The average curves may be used but not with as great accuracy as the individual curves. The degrees of accuracy with which the average curves may be used vary with the concentration and are indicated by the per cent average deviations given for each concentration in Table XXIV.

Examination of the viscosities of damar solutions in toluol indicates that in low concentrations there is very little difference in viscosity, irrespective of the grade used. This condition indicates that there is little change in chemical characteristics with decreasing size of resin particles. In this respect it might be assumed that smaller size particles with increased surface area would be subject to oxidation, resinification, or deresinification reactions on the surface. Above 50 per cent and higher ranges, not only the solubility of the resin in the solvent but also the solubility of the solvent in the resin is important. Higher grades of damar give lower viscosities, and in general lower grades, as indicated by decreasing size and increasing impurities, give higher viscosities. A similar situation holds for petroleum solvents of the hydrogenated as well as the paraffinic type. To state this in another way, since the viscosity-concentration relation is exponential, the differences in viscosities are more apparent at higher concentrations. However, with clean resin, the variation between grades is of a magnitude only slightly greater than the magnitude of experimental error.

The commercial uses of alcohol solutions of Manila resins are of such importance that a separate investigation of the properties of these solutions has been made.[4]

[4] C. W. Kopf, *Paint, Oil Chem. Rev.*, July 21, 1938.

Twenty-seven different commercial varieties and grades of Manila resins were tested for color, viscosity, and solubility in the various alcohols and their denatured modifications. This group consisted of the Macassar manilas (melengket and loba), the pontianaks, the boeas, the Philippine manilas and one Singapore manila.

The alcohols used were the first five aliphatic alcohols: namely, methyl, ethyl, propyl, butyl, and amyl alcohols; Cellosolve (an ether-alcohol); ethylene glycol (a dihydric alcohol); and diacetone alcohol (a ketone-alcohol). Four ethyl alcohols, each with a different denaturant formula, were used. These were Ansol M, Solox, Shellacol, and completely denatured (formula 12). As the propyl alcohol, Petrohol, a 98 per cent technical grade isopropyl alcohol, was used. Ansol M,[5] Solox,[5] Shellacol,[6] and Petrohol[7] are proprietary solvents.

According to the standard solubility test, the manilas are soluble in all of the alcohols mentioned with the exception of ethylene glycol. The resulting solutions are 50 per cent solvent, 50 per cent resin. The colors and viscosities of the Manila resin-alcohol solutions are given in Table XXV.

The viscosity of the solutions is an index of the solvency powers of the solvent. A material which gives a low-viscosity solution is a better solvent than one which results in a higher-viscosity solution.

The boiling points of the alcohols rise with increase in molecular weight. A study of Table XXV reveals that the solvency characteristics of the alcohols for the Manila resins decrease as the boiling point (and the molecular weight) increases, that is, the manilas are less soluble in alcohols of high boiling point than in those showing a lower boiling point. This relation of molecular weight, boiling point, and viscosity is more readily followed in Table XXVI.

The individual characteristics or properties of the various solvents in the same class have a very definite bearing on the resulting solutions. The differences may be slight, but they are nevertheless sufficient to produce distinct effects in the final materials.

Each of the four ethyl alcohols tested had a different denaturant formula; in addition, Ansol M was anhydrous. Each yields solutions of different viscosities. Ansol M shows the greatest solvent action, as indicated by the lower viscosities obtained with it. Table XXVII gives the resulting viscosities for the various grades of pontianak in the four ethyl alcohols.

[5] U. S. Industrial Alcohol Co.
[6] Commercial Solvents Corp.
[7] Standard Alcohol Co.

TABLE XXV

Characteristics of Manila Resin—Alcohol Solutions

	Manila Macassar WS Viscosity	WS Poise	WS Color	Manila Macassar MA Viscosity	MA Poise	MA Color	Loba A Viscosity	A Poise	A Color	Loba B Viscosity	B Poise	B Color	Loba C Viscosity	C Poise	C Color	Loba D Viscosity	D Poise	D Color	Loba DK Viscosity	DK Poise	DK Color	Loba CNE Viscosity	CNE Poise	CNE Color	Loba DUST Viscosity	DUST Poise	DUST Color
Methyl alcohol (methanol)	D	1.00	7	C	0.85	12	E	1.25	5	C	0.85	5	D	1.00	7	B	0.65	10	A-	0.50-	12	A	0.50	9	A-	0.50-	15
Ethyl alcohols																											
Ansol "M"	G	1.65	7	E	1.25	10	J	2.50	4	H	2.00	5	J	2.50	7	E	1.25	9	A	0.50	12	F	1.40	9	A-	0.50-	15
Solox	H	2.00	7	F	1.40	11	M	3.20	4	K	2.75	5	J	2.50	7	F	1.40	9	B	0.65	12	G	1.65	9	A-	0.50-	15
Shellacol	G	1.65	7	G	1.65	12	M	3.20	5	I	2.25	5	I	2.25	6	F	1.40	10	B	0.65	12	F	1.40	9	A-	0.50-	15
Comp. denatured alcohol No. 12	H	2.00	7	H	2.00	11	N	3.40	4	K	2.75	5	I	2.25	6	G	1.65	10	C	0.85	12	H	2.00	9	A-	0.50-	15
Isopropyl alcohol (Petrohol 98%)	M	3.20	7	N	3.40	12	U	6.27	4	T	5.50	5	T	5.50	6	M	3.20	11	H	2.00	12	M	3.20	9	A	0.50	CB
Butyl alcohol (butanol)	R	4.70	8	N	3.40	12	U-V	6.27–8.84	4	V	8.84	5	V	8.84	6	W	10.70	11	I	2.25	12	S	5.00	10	C	0.85	CB
Amyl alcohol, normal	V	8.84	7	U	6.27	12	Y	17.6	4	V	8.84	5	X	12.9	6	W	10.70	11	S	5.00	12	V	8.84	9	E	1.25	CB
Cellosolve	O	3.70	7	O	3.70	12	U-V	6.27–8.84	4	U	6.27	5	U	6.27	6	R	4.70	11	I	2.25	12	T	5.50	10	A	0.50	15
Diacetone alcohol	Y	17.6	7	Y	17.6	CB	Z	22.7	6	Z	22.7	5	Z	22.7	7	Z	22.7	11	W	10.70	CB	Z	22.7	11	H	2.00	CB

	Manila Macassar CBB Viscosity	CBB Poise	CBB Color	Manila Macassar DBB Viscosity	DBB Poise	DBB Color	Philippine Manila Extra bold pale scraped Viscosity	Poise	Color	Philippine Manila Bold pale Viscosity	Poise	Color	Philippine Manila Bold extra pale sorts Viscosity	Poise	Color	Philippine Manila Bold pale chips Viscosity	Poise	Color	Philippine Manila Pale small chips Viscosity	Poise	Color	Philippine Manila Bold amber sorts Viscosity	Poise	Color	Philippine Manila Seeds and dust Viscosity	Poise	Color
Methyl alcohol (methanol)	B	0.65	7	A	0.50	9	H	2.00	4	B-C	0.65–0.85	9	D	1.00	10	A-	0.50-	11	B	0.65	12	A	0.50	13	A-	0.50-	13
Ethyl alcohols																											
Ansol "M"	H	2.00	8	C	0.85	9	I	2.25	5	E	1.25	9	D	1.00	10	A	0.50	11	C	0.85	11	B	0.65	12	B	0.65	13
Solox	H	2.00	8	D	1.00	10	L	3.00	5	G	1.65	9	D	1.00	10	C	0.85	11	D	1.00	12	D	1.00	12	D	1.00	12
Shellacol	I	2.25	8	E	1.25	9	I	2.25	5	G	1.65	9	G	1.65	9	C	0.85	10	C	0.85	10	C	0.85	12	C	0.85	13
Comp. denatured alcohol No. 12	H	2.00	7	G	1.65	9	L	3.00	5	H	2.00	9	J	2.50	10	D	1.00	10	G	1.65	11	F	1.40	13	F	1.40	13
Isopropyl alcohol (petrohol 98%)	O	3.70	8	L	3.00	9	R	4.70	5	O	3.70	9	O	3.70	10	L	3.00	10	I	2.25	11	F	1.40	13	I	2.25	13
Butyl alcohol (butanol)	U	6.27	8	M	3.20	9	T	5.50	6	T	5.50	9	Q	4.35	11	N	3.40	11	O	3.70	11	N	3.40	10	L	3.00	12
Amyl alcohol, normal	X	12.9	7	V	8.84	10	X-Y	12.9–17.6	4	V	8.84	8	W	10.70	10	U	6.27	11	V	8.84	11	T	5.50	12	R	4.70	13
Cellosolve	U	6.27	7	O	3.70	9	T	5.50	5	Q	4.35	9	Q	4.35	10	J	2.50	12	N	3.40	11	K	2.75	13	J	2.50	13
Diacetone alcohol	Z	22.7	8	V	8.84	10	Z	22.7	5	Y	17.6	9	Z	22.7	11	Y	17.6	12	Y	17.6	12	X	12.9	14	Y	17.6	15

	Manila Singapore White split chips Viscosity	Poise	Color	Pontianak Bold scraped Viscosity	Poise	Color	Pontianak Mixed bold Viscosity	Poise	Color	Pontianak Cuttings Viscosity	Poise	Color	Pontianak Nubs Viscosity	Poise	Color	Pontianak Chips Viscosity	Poise	Color	Boea Hard bold white Viscosity	Poise	Color	Boea Hard bold amber Viscosity	Poise	Color	Boea Hard bold dark Viscosity	Poise	Color
Methyl alcohol (methanol)	F	1.40	7	J	2.50	9	D	1.00	8	E	1.25	9	G	1.65	10	A	0.50	13	C	0.85	5	F	1.40	6	A-	0.50-	10
Ethyl alcohols																											
Ansol "M"	F	1.40	7	L	3.00	9	E	1.25	9	I	2.25	9	G	1.65	10	D	1.00	13	D	1.00	6	R	4.70	6	B	0.65	9
Solox	H	2.00	7	R	4.70	9	F	1.40	9	J	2.50	9	I	2.25	10	D	1.00	13	D	1.00	7	U	6.27	6	B	0.65	8
Shellacol	J	2.50	7	U-V	6.27–8.84	9	L	3.00	6	J	2.50	9	H	2.00	10	D	1.00	13	D	1.00	7	V	8.84	5	D	1.00	9
Comp. denatured alcohol No. 12	J	2.50	7	X	12.9	9	Q	4.35	6	O	3.70	9	L	3.00	10	F	1.40	13	N	3.40	5	U	6.27	5	E	1.25	8
Isopropyl alcohol (Petrohol 98%)	R	4.70	7	X	12.9	9	U	6.27	6	U	6.27	9	S	5.00	10	I	2.25	13	I	2.25	6	Y	17.6	6	L	3.00	8
Butyl alcohol (butanol)	U	6.27	6	X	12.9	9	S	5.00	9	V	8.84	9	U	6.27	12	L	3.00	13	V	8.84	5	Z	22.7	6	P	4.00	9
Amyl alcohol, normal	W-X	10.70–12.9	7	Z	22.7	9	Y	17.6	6	Y	17.6	9	X-Y	12.9–17.6	11	V	8.84	13	Z	22.7	6	Z	22.7	6	V	8.84	10
Cellosolve	T	5.50	7	X-Y	12.9–17.6	9	V	8.84	7	V	8.84	9	T	5.50	11	O	3.70	14	U-V	6.27–8.84	5	X	12.9	6	O	3.70	9
Diacetone alcohol	Z1	27.0	7	Z1	27.0	9	Y	17.6	10	Z	22.7	10	Z1	27.0	11	W	10.70	14	P	4.00	8	Z2	36.2	5	S	5.00	11

TABLE XXVI

Alcohol	Molecular Weight	Boiling Point °C.	Viscosities							
			Philippine Bold Pale		Loba A		Boea Hard Bold Amber		Pontianak Cuttings	
			Viscosity	Poise	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise
Methyl	32.03	64.5	B–C	0.65–0.85	E	1.25	F	1.40	E	1.25
Ethyl	48.04	78.5	E	1.25	J	2.50	R	4.70	I	2.25
Isopropyl	60.06	82.3	O	3.70	U	6.27	Y	17.6	U	6.27
Butyl	74.08	117.7	T	5.50	U–V	6.27–8.84	Z	22.7	V	8.34
Amyl	88.09	137.9	V	8.34	Y	17.6	Z	22.7	Y	17.6

Although only pontianaks are cited below, an inspection of Table XXV will show that the greater solvent power of Ansol M is maintained throughout the twenty-seven manilas tested. There are two possible

TABLE XXVII

VISCOSITIES OF PONTIANAKS IN ETHYL ALCOHOLS

Grade	Ansol M		Solox		Shellacol		Completely Denatured No. 12	
	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise
Bold scraped	L	3.00	R	4.70	U–V	6.27–8.84	X	12.9
Mixed bold	E	1.25	F	1.40	L	3.00	Q	4.35
Cuttings	I	2.25	J	2.50	J	2.50	O	3.70
Nubs	G	1.65	I	2.25	H	2.00	L	3.00
Chips	D	1.00	D	1.00	D	1.00	F	1.40

explanations. First, the anhydrous character of the solvent may be a definite advantage, inasmuch as the natural resins do not dissolve in water. A supplementary series of tests, however, proved that water, even to the extent of 5 per cent, could be added to 95 per cent ethyl alcohol without increasing the viscosity of its resin solution or affecting the solubility.

One or more of the denaturants may themselves be excellent solvents for the Manila resins. The character of the alcohol used is again demonstrated to be all important from the viewpoint of the finished solution and the use for which it is proposed.

A comparative scale may be derived for the different grades of each

group of Manila resins according to the viscosity each would have if the same weight of material were dissolved in an equal weight of alcohol. This classification, with the grades of each group arranged in the order of increasing viscosity, is as follows:

Pontianaks
1. Chips
2. Mixed bold
3. Nubs
   Cuttings
4. Bold scraped

Macassar manilas
1. Loba dust
2. Loba DK
3. DBB
   Loba CNE
4. MA
   Loba D
   WS
5. CBB
   Loba B

Macassar manilas (continued)
   Loba C
6. Loba A

Boeas
1. Hard bold dark
2. Hard bold white
3. Hard bold amber

Philippine manilas
1. Bold pale chips
   Seeds and dust
   Bold amber sorts
2. Pale small chips
3. Bold extra pale sorts
4. Bold pale
   Extra bold pale scraped

The above series deals only with the different grades within each class of manilas, and is not an attempt to grade the various classes of Manila resins. In other words, there are four separate classes and each is complete in itself. The pontianaks are listed before the macassars, but this should not be taken to indicate that pontianaks give lower viscosities than do the macassars.

These individual series, although derived from an investigation of the alcohols, may be expected to be maintained with any family of solvents.

In every instance, the Manila resins were insoluble in ethylene glycol, a dihydric alcohol, but were soluble in all the monohydric alcohols. Cellosolve, an ether-alcohol, gave viscosities on a par with those obtained with isopropyl and butyl alcohols. Diacetone alcohol, a ketone-alcohol, gave the most viscous solutions.

For the Philippine manilas, the macassars, and the pontianaks, the best grade produced the greatest viscosity. In the preceding study, the best grade of Batavia damar was found to produce the lowest viscosity. This apparently conflicting behavior bears out a previous observation that damar resins are polymerized by oxidation, whereas Manila resins are depolymerized by oxidation. The better grades of resin are the larger pieces, while the lower grades embrace the smaller sizes. Because of its greater surface area (per unit weight), the smaller piece is

subjected to a greater degree of oxidation than is the larger piece. In the case of damar resins it is the poorer (smaller) grades that give the highest viscosities; but with Manila resins the poorer (smaller) grades give the lowest viscosities.

The data from this investigation permit the preparation of a Manila resin-alcohol solution of any specific viscosity by consulting Table XXV. If the alcohol be restricted to a definite choice, then a grade of resin may be selected from Table XXV. If one grade of resin has been specified, then the table will offer suggestions as to the alcohol best suited to produce the desired results. If there be no restrictions on either resin or alcohol, any combination which will give the solution of required viscosity may be selected.

The entire investigation has indicated the possibilities latent in the solvent when considered from the viewpoint of the finished resin solution. Each distinct solvent of the same class (alcohols) results in a solution of definite and individual characteristics.

Solubility in Alkali. The natural resins are all saponifiable and are therefore soluble in alkali to a more or less degree. The manilas, accroides, and sandarac are soluble to a high degree in sodium carbonate (Na_2CO_3), sodium hydroxide ($NaOH$), ammonium hydroxide (NH_4OH), and other aqueous alkaline solutions and are the only resins which possess commercially important applications in these solutions. Batu and damar are at the other extremity and yield films of maximum alkali resistance.

Those resins possessing a high acid value are more soluble in alkali than resins of lower acid value. The rate of solution in aqueous alkaline solutions is a function of the rate at which the resino-tannols in the resin may be hydrolyzed, and the conditions favoring hydrolysis in the determination of acid value are exceedingly drastic. The natural resins contain organic acids deviating widely in molecular weight so that the acid value, which represents the amount of alkali necessary to react with the carboxyl groups present, does not constitute a direct measurement of the proportions of soluble and insoluble resin constituents. The combination of these factors can be sufficient in certain instances to cause exceptions in which the acid value no longer accurately determines the position of the resin in the scale of alkali solubility.

CHAPTER XIV

COMPATIBILITY WITH OTHER MATERIALS

In this chapter are tabulations of the compatibility of natural resins with a number of other materials. The testing procedure in each case is described.

In the sense of this chapter the natural resins, with the exception of accroides and unrun congo, are compatible with rosin, ester gum, the phenol-formaldehyde (modified and unmodified), and the maleic resins, but not with those of the polystyrene type. Many of them are compatible in solution and in films with nitrocellulose and most of them with ethyl cellulose but not with cellulose acetate. Under the conditions of the test it is not difficult to obtain compatible mixtures with a wide range of oils, waxes, pitches, and asphalts, whereas only a few are miscible with chlorinated rubber or sulfur. The specific nature of cellulose mixed esters is a factor in compatibility. The effect of solvent balances has been discussed under lacquers in Chapter XX.

Compatibility of Natural Resins with Other Resins. Equal amounts of the synthetic and natural resins were employed and the resin to be combined with the natural resin was heated from 400 to 420°F. to convert it into a liquid form. The finely ground natural resin was added in small portions while the temperature was kept at 400 to 420°F. throughout the process. The total time for complete addition of the natural resin was about 5 to 10 minutes. When all the natural resin had been added and completely dispersed, the mixture of the two resins was poured out into a metal container to form a thin cake about ¼ in. thick, and allowed to cool. In order to be termed compatible, the cold cake containing the mixture of resins had to be clear. If it were cloudy, incompatibility was reported.

For the heat-reactive phenol aldehyde resins which gel and solidify at 400 to 420°F., a reverse procedure was employed in which the natural resins were heated to the testing temperature and the ground heat-reactive phenolic aldehyde resin added. Inasmuch as the manilas, congos, and kauris do not melt completely at 400°F., they were not included.

In determining the compatibility of elemi with the polystyrene resin the procedure was slightly modified by heating the two resins together. A determination was also made using dewaxed damar, which

TABLE XXVIII

COMPATIBILITY OF NATURAL RESINS WITH OTHER RESINS

(Ratio 1 to 1)

Natural Resin	100 Per Cent Phenol Alde-hyde Resin	Modi-fied Phenol Alde-hyde Resin	Heat Reac-tive Phenol Alde-hyde Resin	Rosin	Ester Gum	Maleic-Rosin Resin	Para-couma-rone Resin	Poly-styrene Resin
Accroides	I*	I*		I*	I*	C	C	I*
Batavia damar	C	C	C	C	C	C	C	I*
Batu	C	C	C	C	C	C	C	I*
Black east india	C	C	C	C	C	C	C	I*
Boea	C	C		C	C	C	I*	I*
Congo	I*	I*		I*	I*	I*	I*	I
Elemi	C	C	C	C	C	C	C	C
Kauri	C	C		C	C	C	I*	C
Manila loba	C	C		C	C	C	I*	I*
Manila MA	C	C		C	C	C	I*	I*
Manila WS	C	C		C	C	C	I*	I*
Mastic	C	C	C	C	C	C	C	I*
Pale east india Macassar	C	C	C	C	C	C	C	I*
Pale east india Singapore	C	C	C	C	C	C	C	I*
Pontianak	C	C		C	C	C	I*	I*
Sandarac	C	C		C	C	C	I*	I*
Singapore damar	C	C	C	C	C	C	C	I*
Run Batavia damar	C	C	C	C	C	C	C	C
Run batu	C	C	C	C	C	C	C	C
Run black east india	C	C	C	C	C	C	C	I*
Run boea	C	C	C	C	C	C	C	I*
Run congo	C	C	C	C	C	C	C	C
Run kauri	C	C	C	C	C	C	C	C
Run manila loba	C	C	C	C	C	C	C	I*
Run manila MA	C	C	C	C	C	C	C	I*
Run manila WS	C	C	C	C	C	C	C	I*
Run pale east india Macassar	C	C	C	C	C	C	C	C
Run pale east india Singapore	C	C	C	C	C	C	C	I*
Run pontianak	C	C	C	C	C	C	C	I*
Run singapore damar	C	C	C	C	C	C	C	C

* Disperses but cloudy.

C Compatible I Incompletely compatible

was found to be compatible with the polystyrene resin. Where incompatibility of run resins was encountered at the specified temperature, higher temperatures were used. It was found that the thermally processed manila grades could be made completely compatible at tempera-

tures ranging from 500 to 600°F. The run east indias also become compatible at temperatures of about 600°F.

Compatibility of Natural Resins with Nitrocellulose. This testing concerned itself largely with the working out of solvent balances. The

TABLE XXIX

COMPATIBILITY OF NATURAL RESINS WITH NITROCELLULOSE

Resin	Solvent									Nitrocellulose: Resin			Per Cent Total Solids
	Butanol	Butyl Acetate	Cellosolve	Ethyl Acetate	High Flash Naphtha	Ethanol	Methanol	Toluol	Xylol	2:1	1:1	1:2	
Accroides		40		40		20				C	C	C	
Batavia damar		80			20					C	C	C	20
Batu	10			35				55		VSI*	VSI*	VSI*	20
Boea	60		20				20			C	C	C	16⅔
Congo ester	40	20							40	VSI	VSI	VSI	20
Dewaxed damar		80			20					C	C	C	20
Elemi		80			20					C	C	C	20
Kauri, brown	20	20					60			C	C	C	16⅔
Kauri, pale	20	20					60			C	C	C	16⅔
Manila	60		20				20			C	C	C	16⅔
Manila CBB	60		20				20			C	C	C	16⅔
Manila DBB	60		20				20			C	C	C	16⅔
Manila loba	60		20				20			C	C	C	16⅔
Mastic		80			20					C	C	C	20
Pale east india Macassar	10			35				55		VSI*	VSI*	VSI*	20
Pale east india Singapore	10			35				55		VSI*	VSI*	VSI*	20
Pontianak	60		20				20			C	C	C	16⅔
Sandarac			100							VSI	VSI	VSI	16⅔
Singapore damar		80			20					C*	C*	C*	20
Run congo	60	25							15	C	C	C	20
Run black east india		80			20					I	I	I	20
Run boea		80			20					VSI	VSI	VSI	20
Run damar		80			20					VSI	VSI	VSI	20
Run kauri		80			20					VSI	VSI	VSI	20
Run manila		80			20					VSI	VSI	VSI	20

* Compatible when "dewaxed"
C Compatible VSI Very slightly incompatible I Incompatible

combinations were made by placing the cellulose derivative, natural resin, and the solvent combination in a bottle and dissolving on an end-over-end mixer. The nitrocellulose used was RS half-second; the ratios of nitrocellulose to resin, 2 to 1, 1 to 1, and 1 to 2. The resulting unplasticized lacquers were flowed on to glass panels and allowed to dry. Haze-free, clear, transparent films were reported as compatible; otherwise, incompatibility was indicated.

Compatibility of Natural Resins with Ethyl Cellulose. The procedure here was the same as with nitrocellulose except that low-viscosity ethyl cellulose was used in place of the nitrocellulose.

TABLE XXX

COMPATIBILITY OF NATURAL RESINS WITH ETHYL CELLULOSE

Resin	Solvent								Ethyl Cellulose: Resin			Per Cent Total Solids
	Benzol	Butanol	Butyl Acetate	Ethanol	High Flash Naphtha	Methanol	Toluol	Xylol	2:1	1:1	1:2	
Accroides				20			80		SI	I	I	20
Batavia damar		20	40		40				C	C	C	20
Batu		16						90	VSI	VSI	VSI	15.8
Black east india				20			80		I	I	I	20
Boea		50		10			40		C	C	C	20
Congo ester		16						90	VSI	VSI	VSI	15.8
Dewaxed damar				20			80		C	C	C	20
Elemi				20			80		C	C	C	20
Kauri, brown	55	20				25			C	C	C	20
Kauri, pale	55	20				25			C	C	C	20
Manila		50		10			40		C	C	C	20
Manila CBB		50		10			40		C	C	C	20
Manila DBB		50		10			40		C	C	C	20
Manila loba		50		10			40		C	C	C	20
Mastic		50		10			40		C	C	C	20
Pale east india Macassar		16						90	VSI	VSI	VSI	15.8
Pale east india Singapore		16						90	VSI	VSI	VSI	15.8
Pontianak		50		10			40		C	C	C	20
Sandarac		20		15			65		C	C	C	20
Singapore damar		20	40		40				C	C	C	20
Run congo				20			80		C	C	C	20
Run black east india				20			80		I	I	I	20
Run boea				20			80		VSI	VSI	VSI	20
Run damar				20			80		C	C	C	20
Run kauri				20			80		C	C	C	20
Run manila				20			80		C	C	C	20

C Compatible SI Slightly incompatible
I Incompatible VSI Very slightly incompatible

Compatibility of Natural Resins with Cellulose Acetate. Cellulose acetate is noted for its limited solubility in solvents. As a result, the testing method for resin compatibility had to be limited to acetone and dioxane, both of which have limitations as solvents for the natural resins. The procedure was similar to that described for nitrocellulose.

Successful combinations of accroides and cellulose acetate are tabulated on page 158. All parts are by weight.

The compatibilities tested and tabulated here deal with films laid down from solutions rather than miscibility in molded products. Better compatibilities of the natural resins are obtained with the cellulose acetate butyrate and cellulose acetate propionate whose solubilities of themselves are greater in a wider range of solvents.

TABLE XXXI

COMPATIBILITY OF NATURAL RESINS WITH CELLULOSE ACETATE

Resin	Solvent					
	Acetone			Dioxane		
	2:1	1:1	1:2	2:1	1:1	1:2
Accroides				C	C	C
Batavia damar				I	I	I
Batu	I	I	I	I	I	I
Boea	I	I	I			
Black east india	I	I	I	I	I	I
Elemi				SI	SI	SI
Kauri, brown	I	I	I			
Kauri, pale	I	I	I			
Manila CBB	I	I	I			
Manila loba	I	I	I			
Manila WS	I	I	I			
Mastic				SI	SI	SI
Pale east india Macassar				I	I	I
Pale east india Singapore				I	I	I
Philippine manila	I	I	I			
Pontianak	I	I	I			
Sandarac				SI	SI	SI
Singapore damar				I	I	I
Run Batavia damar				I	I	I
Run black east india				I	I	I
Run boea				I	I	I
Run congo				I	I	I
Run kauri				I	I	I
Run Philippine manila				I	I	I

I Incompatible C Compatible SI Slightly incompatible

TABLE XXXII

Ratio of Cellulose Acetate to Accroides	2 to 1	1 to 1	1 to 2
Accroides	8	14	20
Cellulose acetate	16	14	10
Dioxane	76	77	70
Per cent solid content	24	27	30
Clarity of mixture	Clear	Clear	Clear
Clarity of dry film	Clear	Clear	Clear

Compatibility of Natural Resins with Oils. Equal weights of the resin and oil were heated to 400 to 420°F., with the oil brought up to temperature and the ground resin added in small amounts during a heating period of 5 to 10 minutes. The cold resin-oil mixture was examined for homogeneity.

TABLE XXXIII

COMPATIBILITY OF NATURAL RESINS WITH OILS

(All ratios)

Resin	Blown Castor	China Wood	China Wood Oil Substitute	Fish	Hempseed	Linseed	Oiticica	Rapeseed	Soybean	Sunflower
Accroides	I	I	I	I	I	I	I	I	I	I
Batavia damar	C	C	C	C	C	C	C	C	C	C
Batu	C	C	C	C	C	C	C	C	C	C
Black east india	C	C	C	C	C	C	C	C	C	C
Elemi	C	C	C	C	C	C	C	C	C	C
Mastic	C	C	C	C	C	C	C	C	C	C
Pale east india Macassar	C	C	C	C	C	C	C	C	C	C
Pale east india Singapore	C	C	C	C	C	C	C	C	C	C
Sandarac	I	I	I	I	I	I	I	I	I	I
Singapore damar	C	C	C	C	C	C	C	C	C	C
Run boea	C	C	C	C	C	C	C	C	C	C
Run congo	C	C	C	C	C	C	C	C	C	C
Run kauri	C	C	C	C	C	C	C	C	C	C
Run manila	C	C	C	C	C	C	C	C	C	C
Run manila loba	C	C	C	C	C	C	C	C	C	C
Run pontianak	C	C	C	C	C	C	C	C	C	C

C Compatible I Incompatible

Compatibility of Natural Resins with Waxes. Equal weights of the wax and resin were heated together at temperatures indicated in the tables. Homogeneous mixtures were reported as compatible, and show solubility in the liquid and solid phases.

TABLE XXXIV

COMPATIBILITY OF NATURAL RESINS WITH WAXES

(Ratio of resin to wax, 1:1)

Resin	Beeswax	Carnauba	Japan	Montan	Ozokerite	Paraffin	Petrolatum Wax and Paraffin*	Stearic Acid
Accroides	P.C.	P.C.						P.C.
Batavia and Singapore damar	C-1	C-1	C-1	C-1	C-1	C-2	C-4	C-1, 2
Batu	C-2	C-3	C-3	C-3	C-3	C-3	C-4	C-2
Black east india	C-2	C-2	C-2	C-2	C-2	C-2	C-4	C-2
Congo	C-5	C-5	P.C.	C-5	P.C.	P.C.	P.C.	C-3
Elemi	C-1	C-1	C-1	C-1	C-1	C-1	C-1	C-1
Kauri	C-5	C-5	C-5	C-5	P.C.	C-5	C-5	C-2
Pale east india	C-2	C-2	C-2	C-2	C-2	C-3	C-4	C-2
Manila WS	C-5	C-5	P.C.	C-5	P.C.	P.C.	P.C.	C-2
Manila loba	C-5	C-5	C-5	C-5	P.C.	P.C.	P.C.	C-2
Mastic	C-1							C-2
Run congo	C-2	C-2	C-2	C-2	P.C.	P.C.	P.C.	
Run kauri	C-2	C-2	C-2	C-2	C-2	C-2	C-2	C-2
Run manila	P.C.					P.C.		

* 45% Petrolatum wax, 10% paraffin, balance resin.
C-1 Compatible at temperatures in the range of 90–120°C.
C-2 Compatible at temperatures in the range of 120–150°C.
C-3 Compatible at temperatures in the range of 150–200°C.
C-4 Compatible at temperatures in the range of 200–225°C.
C-5 Compatible at temperatures in the range of 275–325°C.
P.C. Partially compatible.

Compatibility of Natural Resins with Asphalts and Pitches. Equal weights of the resins and the asphalt or pitch under test were heated together at temperatures between 350 and 450°F., except in the case of elemi where the temperature was 230°F., for 5 minutes, then poured out into thin slabs and examined for homogeneity.

Compatibility of Natural Resins with Chlorinated Rubber. Cold-cut solutions in various solvents were made containing 40 per cent of resin. These were mixed with 20 per cent solutions of chlorinated rubber to give chlorinated rubber-resin ratios of 2 to 1, 1 to 1, and 1 to 2. Haze-free films on glass indicated compatibility.

TABLE XXXV

COMPATIBILITY OF NATURAL RESINS WITH ASPHALTS AND PITCHES

Resin	Petroleum Asphalt	Coal Tar Pitch	Gilsonite	Stearin Pitch	Vegetable Pitch
Accroides	I	I	I	I	I
Batavia damar	C	C	C	C	C
Batu	C	C	SI	C	C
Black east india	C	C	SI	C	C
Boea	I	C	I	I	C
Congo	I	I	I	I	C
Congo ester	C	C		C	C
Elemi	C	C	C	C	C
Kauri, brown	I	C	I	I	C
Kauri, pale	I	C	I	I	C
Manila CBB	I	C	I	I	C
Manila loba	I	C	I	I	C
Manila WS	I	C	I	I	C
Mastic	C	C	C	C	C
Pale east india Macassar	C	C	SI	C	C
Pale east india Singapore	C	C	SI	C	C
Philippine manila	I	C	I	I	C
Pontianak	I	C	I	I	C
Sandarac	I	C	I	I	C
Singapore damar	C	C	C	C	C
Run Congo	C	C	C	C	C
Run kauri	C	C	C	C	C
Run manila CBB	C	C	C	C	C

C Compatible I Incompatible SI Slightly incompatible

Compatibility of Natural Resins with Sulfur. Equal weights of sulfur and resin in ground condition were mixed and heated from 310 to 320°F. The mixtures were then cast and the slabs examined to determine homogeneity. Homogeneous mixtures were termed dispersions or compatible.

Compatibility with Mixed Cellulose Esters. Combinations of resins with mixed cellulose esters such as those of acetic, butyric, and propionic acids are of industrial importance.

Fordyce, Salo, and Clarke[1] have studied the cellulose mixed esters in the hope of obtaining compositions possessing the desirable characteristics of cellulose acetate films together with the improved solubility in solvents and compatibility with resins found in the higher cellulose

[1] C. R. Fordyce, M. Salo, and G. R. Clarke, *Ind. Eng. Chem.*, **28**, 1310-13 (1936).

TABLE XXXVI

COMPATIBILITY OF NATURAL RESINS WITH CHLORINATED RUBBER

	Benzol			Hi-Flash Naphtha			Ethyl Acetate			Butyl Acetate			Octyl Acetate			Methyl Ethyl Ketone		
Ratio of Chlorinated Rubber to Resin*	2 : 1	1 : 1	1 : 2	2 : 1	1 : 1	1 : 2	2 : 1	1 : 1	1 : 2	2 : 1	1 : 1	1 : 2	2 : 1	1 : 1	1 : 2	2 : 1	1 : 1	1 : 2
Accroides										I	I	I						
Batavia damar	C	C	C	C	C	C												
Batavia damar, dewaxed	C	C	C	C	C	C												
Pale east india, Macassar	I	I	I	I	I	I												
Batu	I	I	I	I	I	I												
Mastic							C	C	C	C	C	C	C	C	C	C	C	C
Elemi							C	C	C	C	C	C	C	C	C	C	C	C
Kauri, brown							I	I	I	I	I	I				I	I	I
Manila loba							I	I	I	I	I	I				I	I	I
Sandarac							I	I	I	I	I	I				I	I	I
Black east india				I	I	I												
Boea										I	I	I						
Run black east india				SI	SI	SI												
Run boea				SI	SI	SI												
Run congo	C	C	C	SI	C	C	I	I	I	C	C	C	C	C	C			
Run damar	C	C	C	C	C	C												
Run manila				SI	SI	SI												

* 40% Solutions of resin were used with 20% solutions of chlorinated rubber.

C Compatible I Incompatible SI Slightly incompatible

TABLE XXXVII

Compatibility of Natural Resins with Sulfur

Ratio of Resin to Sulfur	1:1	3:1	9:1	12:1	19:1
Batavia damar	C	Cloudy	Cloudy	Clear hot, cloudy cold	Clear
Singapore damar	C	Cloudy	Cloudy	Clear hot, cloudy cold	Clear
Black east india	N.C.				
Batu	N.C.				
Pale east india	N.C.				
Manila	N.C.				
Congo	N.C.				
Congo ester	N.C.				
Kauri	N.C.				
Elemi	Dispersion				
Mastic	Dispersion				
Sandarac	N.C.				

C Compatible N.C. Incompatible

esters. The higher esters investigated were cellulose acetopropionate and cellulose acetobutyrate. It was found that the few resinous materials compatible with cellulose acetate exhibited as good or better compatibility with the higher esters. In systems of mixed esters certain resins, showing complete incompatibilty with cellulose acetate, can be incorporated with clear, homogeneous films resulting.

The cellulose mixed ester systems were graphically represented upon triangular coordinate charts in which the variables were the proportions of unesterified hydroxyl groups and the hydroxyl groups esterified by each of the two acids. Graphs in Fig. 26 show the amounts of damar and elemi compatible with the varying compositions of cellulose mixed esters.

The solvent employed in determining the areas of compatibility was as follows: methyl acetate, 10 per cent; 1, 4-dioxane, 20; ethyl alcohol, 20; butanol, 10; and toluol, 40. In areas of limited solubility the solvent mixture was varied by addition of methyl acetate. Resins to be tested were added in amounts equivalent to 25, 50, and 75 per cent of the cellulose ester content. Only films showing no sign of haze or bloom were designated as compatible. The damar used was dewaxed by addition of methanol to a solution of the resin.

Miscellaneous Materials. Data on compatibility of the various resins with other cellulose derivatives such as benzyl cellulose which is solvent soluble, and methyl cellulose which is water soluble, or the hydroxy ethyl celluloses, are incomplete and are therefore not tabulated.

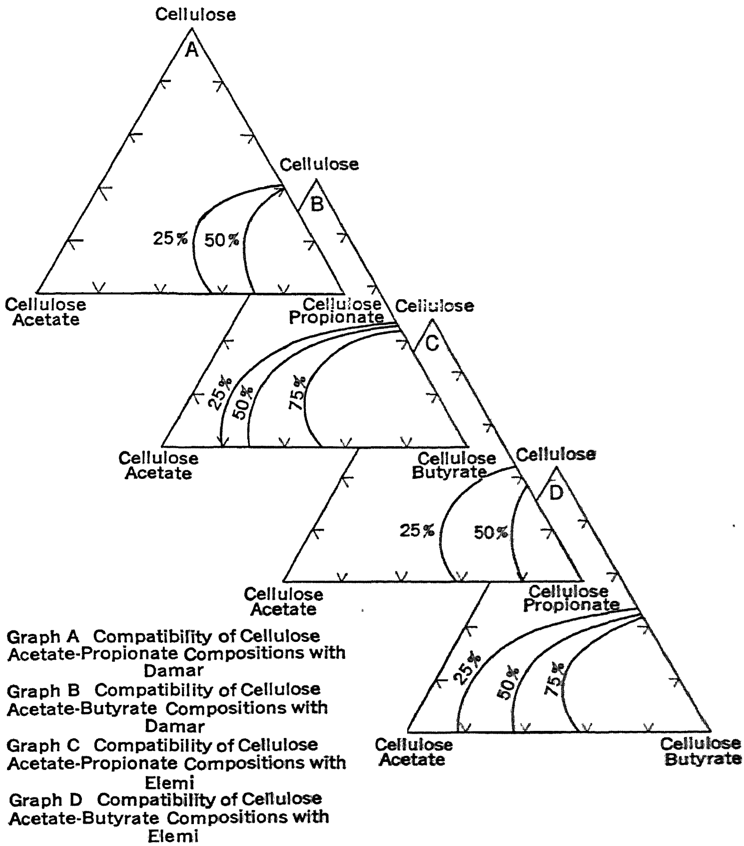


FIG. 26. Compatibility of damar and elemi with cellulose mixed esters.

Application of the test methods outlined in this chapter affords an easy determination of mutual solubility and compatibility of other products, both natural and synthetic, with the natural resins. In general those materials which show water solubility may be classified as incompatible with the resins, unless compatibility in emulsions be considered a special case.

CHAPTER XV

THERMAL PROCESSING

The natural resins may be divided into a number of different classes according to the degree of thermal processing needed to make them oil soluble. The behavior when subjected to thermal treatment, often called "running," "melting," or "cracking," varies considerably for different types of resin.

In the first class accroides may be listed, inasmuch as it is not possible to make this resin compatible with oils by heating. Because of what may be termed its "heat-reactive" qualities, attempts to convert accroides to an oil-soluble form by heat treatment have always yielded a hard, insoluble, and infusible mass.

In the second class are grouped mastic and sandarac, which are seldom used for oil varnishes and find their main applications when dissolved in solvents.

In the third class is elemi, which can be incorporated in varnish oils at temperatures low enough to forestall any destructive decomposition of the resin.

In the fourth class are the damars such as Batavia and Singapore. These, like elemi, are already oil soluble in their normal state and can be dissolved in oil simply by heating in the oil itself. This treatment yields a stable varnish in which the resin remains soluble upon cooling. The only loss encountered is that due to the evaporation of moisture and the evolution of volatile oils. The temperatures used do not cause chemical breakdown of the resin's components and need only be high enough to melt the damar in the oil.

In the fifth class are the pale east indias of Macassar and Singapore packings, black east india, and batu. These may be directly dissolved in varnish oils, in the same manner as the damars, without pretreatment, although slightly higher temperatures and longer heating periods are necessary. However, varnishes prepared by this method are of uncertain stability and, unless the varnish maker has had experience in the preparation of such varnishes, it is better practice to process the resin separately. When so processed, the resin is heated in a vessel until a homogeneous, thin liquid, free of lumps or gummy masses, is obtained. A suggested procedure for an average-sized batch (100 lb.) of resins of

this class is to heat the resin so that a temperature of 600°F. is reached in about 1 to 1¼ hours. Holding the batch at this temperature for about ½ hour will permit the foaming mass to subside to a liquid. The liquid resin should drip from the paddle in the manner of hot oil. This procedure may be modified by the varnish technician for making varnishes of special types. For East India resins, particularly when processed for flat varnishes, somewhat less simple methods involving steplike operations (repeated heatings and coolings) may be desired for definite types of results.

In the sixth class are resins which cannot be directly incorporated with oils, but which need to be processed in advance. After processing, hot oil may be added and the heating continued to form the varnish, or the resin may be allowed to cool, be dissolved in a solvent, and the solvent mixture of the resin may be incorporated with a previously bodied oil. In American practice the first method is preferred, as the latter does not permit the desirable interreactions between oil and resin. In this class are kauri, boea, and pontianak, all of which may be processed in a similar manner. A suggested procedure involves heating the resins to a temperature of 600°F. over a time period of about 1¼ hours and holding at that temperature for about ½ hour until all lumps, spongy or gummy masses, and all or nearly all the foam have disappeared. Another suggested method for kauri, boea, and pontianak would be to heat the resins to 625°F. in about an hour, with occasional stirring. They are then allowed to cool to 500 to 550°F., again are brought up to 600°F., and are held for about ½ hour until they drip cleanly from the paddle in the manner of hot oil.

The soft Manila melengkets and the half-hard Manila lobas are more often employed in spirit varnishes than in oil-base vehicles. These resins may be processed in a manner similar to that described for pontianak, although the lobas do not "run" quite so easily, making it necessary to employ a longer heating period. This also applies to the CBB and DBB manilas, which are actually mixtures of boea and loba.

In the seventh class are to be found those fossil resins which are hard and totally insoluble. These need to be drastically processed before they can be incorporated with oils. Congo is an example of this class of resins. A suggested processing method involves heating a normal-sized batch (100 lb.) in an average varnish kettle to 600°F. over a period of one hour. The resin should then be held at 600°F. until all the hard lumps of resin have disappeared and the mass is in a plastic condition. This may take an hour. Occasional stirring avoids local overheating. With the expiration of this period, the foam will have begun to sub-

side. The temperature should be raised to 650°F. and held until the resin is liquid and shows a clean drip from the paddle. This final operation takes about 15 minutes. In another and faster method, the resin is heated to 650°F. in about 1½ hours and held at that temperature for about ½ hour until it is completely oil soluble.

There are two general methods of running in reference to the equipment employed. During the running operation, volatile oils are distilled off in variable quantities depending upon how the procedure is carried out. If the cover be left on the kettle (closed-kettle running), a larger amount of the volatile oils is retained and the resin becomes oil soluble with a minimum loss of weight. The upper sections of the kettle act as a condenser, since they are cooler than the bottom. In the other method (open-kettle running), no cover is used. Any material volatilized during the operation is allowed to escape without condensation.

In general, the varnishes prepared from resins thermally processed in closed kettles are not quite so hard as those prepared in an open kettle with their greater loss of volatile matter. This, however, holds true only if the difference in running method is the only variable in the varnishes under comparison.

The loss in weight of resin upon running is a function of the type of resin, the rate of heating, the duration of the heating, the method of running, the temperature used, and the variety of equipment which may be employed. The loss in weight may vary from about 10 per cent for such resins as the east indias, to as high as 35 per cent (under special circumstances) for resins which are more difficult to run. For the latter (congo, kauri, and manila), 25 per cent may be considered as an average loss in normal practice.

Thermal processing is a tool enabling the varnish maker to impart a wide range of properties to resinous materials so that these may fit special requirements. For example, specifications of the United States Government exist calling for congo to be run to the abnormally high loss of 40 per cent for use in varnishes where excellent adhesion to metal is desired.

Because of the many variable factors entering into the running operation, it is impossible to present here an iron-bound procedure for any one of the resins. The duration, rate of heating, and temperatures will vary from plant to plant, depending upon the facilities available as well as the particular use to which the run resin is to be put. Running procedures used by the authors are summarized in Table XXXVIII. The suggested procedures apply to open-kettle runs. For closed kettles,

TABLE XXXVIII

RECOMMENDED RUNNING PROCEDURES

Resin	Processing Method	Normal Loss per Cent by Weight
Black east india Pale east india Batu	Heat to 600°F. in 1¼ hrs. and hold at this temperature until oil soluble (about 1½ hrs.).	12–20
Boea Pontianak Philippine manila	Heat to 600°F. in 1¼ hrs. and hold at this temperature until oil soluble (about ½ hr.). or Heat to 625°F. in 1 hr. Allow to cool to 500 to 550°F. and then bring to 600°F. Hold at this temperature until oil soluble (about 1 hr.).	20–25
Manila CBB Manila DBB	Heat to 600°F. in 1¼ hrs. and hold at this temperature until oil soluble (about 2 hrs.).	25
Manila loba	Heat to 600°F. in 1 to 1¼ hrs. and hold at this temperature until oil soluble (about 2 hrs.).	30
Manila melengkets	Heat to 600°F. in 1¼ hrs. and hold at this temperature until oil soluble (about ½ hr.).	30
Kauri	Heat to 600°F. in 1¼ hrs. and hold at this temperature until oil soluble (about ½ hr.). or Heat to 625°F. in 1 hr. Allow to cool to 500 to 550°F. and then bring to 600°F. Hold at this temperature until oil soluble (about 1 hr.).	20–25
Congo	Heat to 650°F. in 1½ hrs. and hold at this temperature until oil soluble (about ½ hr.). or Heat to 600°F. in about 1 hr. Hold at this temperature until the resin is plastic and all the hard lumps have been disintegrated and the foam has begun to subside (about 1 hr.). Stir occasionally to avoid overheating. Raise temperature to 650°F. and hold until all the resin is liquid and oil soluble (about ½ hr.).	20

lower weight losses and somewhat shorter heating periods may be expected.

The Chemistry of Thermal Processing. Through the efforts of numerous investigators, a clear picture of the chemical change involved in the running of natural resins is gradually being assembled.

The first scientific investigations of running were devoted, for the most part, to the examination of the oily distillate which was obtained as a product of the decomposition. Schleider[1] recorded the presence of water in the liquid obtained from the running of copals. Freidburg[2] reported, without amplification, detection of the odor of limonene while running a copal. The work of Wallach[3] was more definite, and the identification of pinene and limonene in a kauri distillate was achieved. Similar results were obtained by Guedras.[4] Tschirch[5] found formic, acetic, and succinic acids in the distillate from certain hard copals. Westenberg,[6] by decomposition of congo at 300°C., obtained an oil, the greater part of which distilled between 240 and 260°C. This fraction was not identified as any specific chemical compound, but was stated to be extremely reactive. By dehydrogenation with selenium, Westenberg subsequently isolated a hydrocarbon, $C_{13}H_{14}$, which he recognized as trimethyl naphthalene.[7] This compound was also obtained in an investigation on manila performed by Ruzicka, Steiger, and Schinz.[8] Trost and Debelli,[9] in an examination of the neutral fraction of copal oil isolated two hydrocarbons, $C_{14}H_{22}$ and $C_{18}H_{28}$. The former, a bicyclic compound, was recognized as tetramethyl naphthalene with three methyl groups at the 1, 2, and 5 positions and the fourth at either the 4 or 9 position. The latter was a tricyclic compound possessing three double bonds. On dehydrogenation both yielded $C_{10}H_5(CH_3)_3$. Each absorbed oxygen but had no drying properties.

A number of interesting observations were made by Richmond[10] and Brooks[11] after their examination of manilas. Richmond reported the presence of a number of compounds in the distillate obtained by heating

[1] *Ann.*, **113**, 338 (1860).
[2] *J. Am. Chem. Soc.*, **12**, 285 (1890).
[3] O. Wallach, *Ann.*, **271**, 308 (1892).
[4] *Chem.-Ztg.*, **26**, 1132 (1902).
[5] A. Tschirch, *Arch. Pharm.*, **240**, 202 (1902).
[6] L. Westenberg, *Rec. trav. chim.*, **48**, 580 (1929).
[7] L. Westenberg, *Rec. trav. chim.*, **50**, 188 (1931).
[8] L. Ruzicka, R. Steiger, and H. Schinz, *Helv. Chim. Acta*, **9**, 962-78 (1926).
[9] *Ann. chim. applicata*, **26**, 301 (1936).
[10] G. F. Richmond, *Philippine J. Sci.*, **5A**, 177 (1910).
[11] B. T. Brooks, *Ibid.*, **5A**, 203 and 219 (1910).

this resin to 330°C. The following were listed: carbon dioxide, water, formic and acetic acids, formic, acetic, and furfuryl aldehydes, methanol, acetone, various terpenic bodies (pinene, β-pinene, limonene, dipentene, and camphene), as well as a "resin oil" and a quantity of gaseous hydrocarbons. Richmond was unable to detect any appreciable difference in the acids remaining in the run resin when compared to those in the original, and concluded that heat had no effect upon the acid constituents.

Brooks suggested that the acidity of the varnish oil and the presence of free copal oil are important factors in the satisfactory solution of the resin. If the copal oil were removed by vacuum as soon as it had formed, the run resin proved to be much less oil soluble than would otherwise be true. On carrying his work further, Brooks found the presence of fatty acids to be unnecessary, provided sufficient copal oil were present. In this manner, a stable varnish using mineral oil in place of vegetable oil was prepared, although if the latter had been used, a less severely run resin would have been satisfactory. Apparently the presence of free fatty acids and free copal oil permits the manufacture of oil varnishes with less decomposition of the resin.

Wolff,[12] in an investigation of the chemical changes occurring during the running of manila, proved that the copal oil obtained consisted of resin acids and unsaponifiable substances together with small quantities of aldehyde and formic and acetic acids. In addition, the presence of traces of carbon monoxide was noted. Comparison of the acid and saponification values of the products with those of the original resin led him to conclude that running is essentially a decarboxylation process with carbon dioxide and hydrocarbon oils as its by-products. A well-defined ratio existed between the amount of carbon dioxide formed and the reduction in resin acidity.

Kroll,[13] engaged in research on a sample of soft manila, succeeded in isolating dibasic acids which, upon heating, were changed to the monobasic form with the evolution of carbon dioxide. With continued heating, a hydrocarbon was obtained.

Ruzicka, Steiger, and Schinz,[14] from their study of manila, concluded that the critical point in the copal running process was that at which the dicarboxylic acids were decomposed. These workers observed that

[12] H. Wolff, *Farben-Ztg.*, **29**, 2039 (1924).

[13] N. Kroll, Dissertation Kiel (1925); Horrman and Kroll, *Arch. Pharm.*, **265**, 214 (1927).

[14] L. Ruzicka, R. Steiger, and H. Schinz, *Helv. Chim. Acta*, **9**, 962-78 (1926).

the dibasic acids were not soluble in varnish oils while their monobasic forms were.

The theory that the process consists essentially of decarboxylation of dibasic acids to their monobasic form with the liberation of carbon dioxide was investigated by Hellinckx,[15] in a specially designed apparatus. A schematic diagram of his experimental setup is given in Fig. 27.

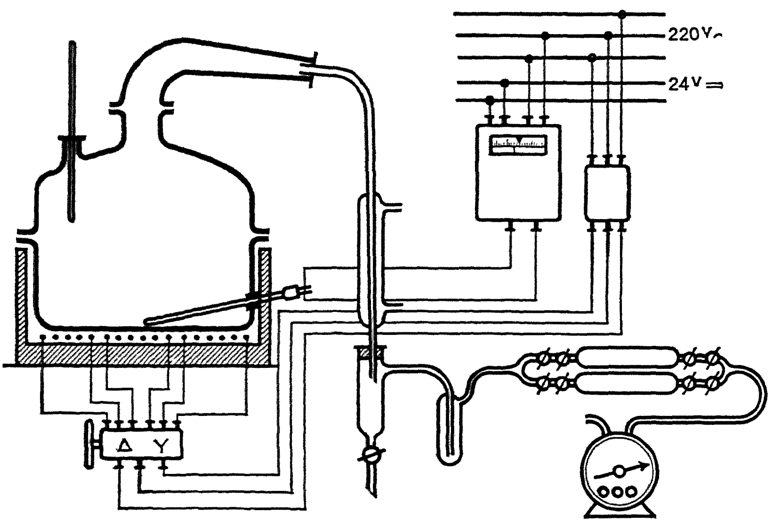


FIG. 27. Schematic diagram of Hellinckx apparatus.

The running pot was of stainless steel, 50 cm. (about 20 in.) in diameter and 40 cm. (about 16 in.) in total height. The resin was treated in batches of 2 kg. (about 4.4 lb.) spread out in a layer a few centimeters thick. Heating was carried out in an electrically heated air bath with a pyrometer immersed in the resin mass and connected to an automatic temperature regulator.

The top of the vessel carried a curved pipe for the removal of gases and vapors. These were led through a spiral condenser which condensed the vapors into a reservoir from which they were drawn off. Traces of water or copal oil that escaped condensation were held back by an ice-enclosed trap. The non-condensable gases were then passed through two gas burets arranged in parallel, one being in use while the other was being replaced. The circuit ended in a gas meter.

[15] L. Hellinckx, "La Pyrogenation du Copal Congo," Bruxelles, Librairie Falk fils, George Van Campenhout, Successeur, 22, Rue des Paroissiens, 22 (1938).

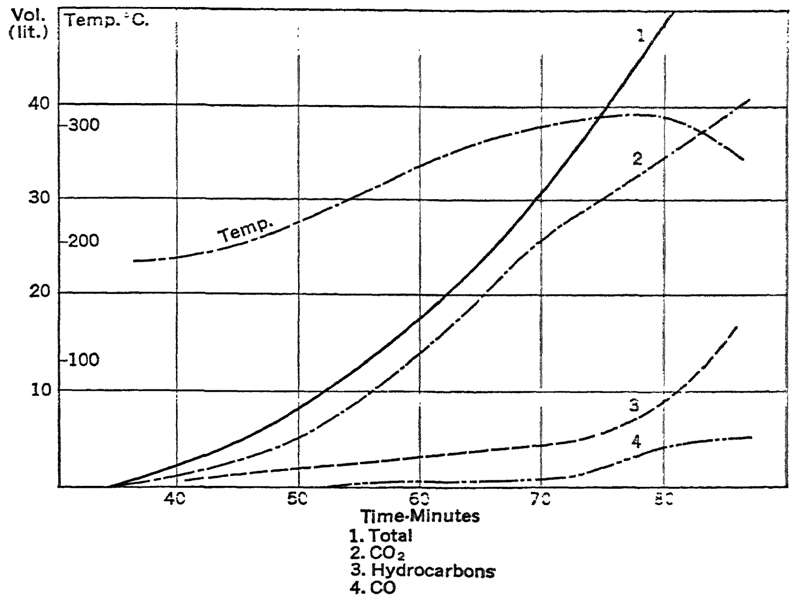


FIG. 28. Evolution of gases during experiment 1. (Hellinckx)

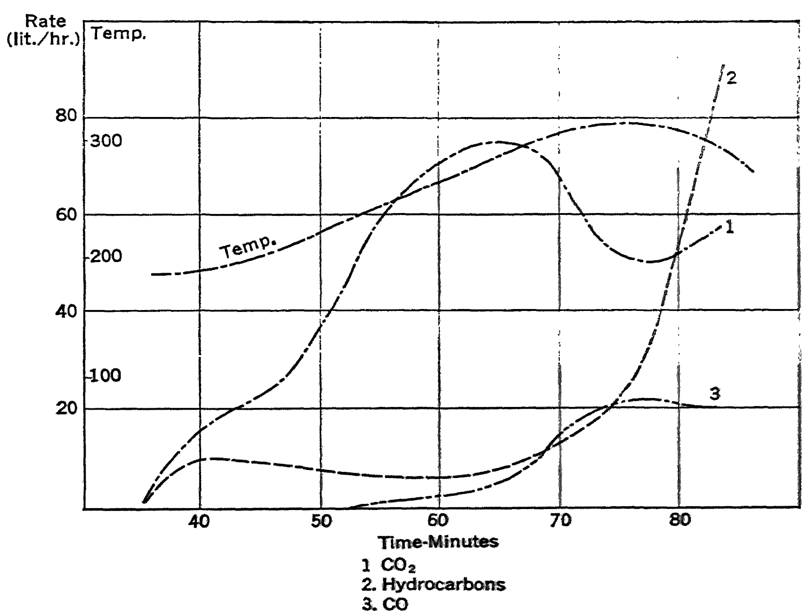


Fig. 29. Instantaneous rates of evolution of gases during experiment 1. (Hellinckx)

TABLE

EXPERIMENTS ON

Experiment Number	Heat Treatment				Properties	
	Up to 300°C. (*min.*)	Held at 300°C. (*min.*)	Above 300°C. (*min.*)	Loss in weight (*per cent*)	Appearance	Melting point °C.
Original resin	..	..	..	..	Colorless	119
1	70	15	..	..	Yellow-brown	59
2	130	40	50 at 310°	12.1	Incompletely run*	..
3	50	70	15 at 320°	12.1	Brown-yellow	79
4	60	..	In 80 to 370°	18.5	Dark brown	..
5	80	60	In 50 to 360°	16.5	Brown, sticky	..
6	90	60	In 30 to 350°; 50 at 350°	20.0	Dark brown, sticky	..
7	90	70	..	10.7	Yellow	79

* Figures enclosed in parentheses refer to run portions.

The congo was heated under prearranged conditions and the changes occurring in the resin followed by analysis of the gases and distillates formed. Various grades of congo were so processed. Data on white congo are given in Table XXXIX.

The composition and volume of the gases evolved during running furnished information as to the character of the decomposition. Curves showing the evolution of total and individual gases in one of the runs are given as Figs. 28 and 29. Fig. 28 shows the total volumes obtained and Fig. 29 charts the instantaneous rate of evolution. These curves were for a white Congo resin which had been taken to 300°C. in 75 minutes and held at that temperature for 10 minutes. The data are given in Table XL.

Hellinckx concluded that the decomposition of Congo resin takes place in three different principal forms: (1) decarboxylation of dibasic acids to their monobasic form, as indicated by the evolution of carbon dioxide and the decrease in acid value of the run resin; (2) cracking, as indicated by the formation of gaseous hydrocarbons and oily distillates; (3) reactions responsible for the liberation of carbon monoxide, involving the transformation of hydroxy acids to anhydrides and ketones.

XXXIX

WHITE CONGO

of The Run Resin					Gas Evolved			Distillate	
Density	Acid number	Saponification number	Iodine number	Acetyl number	CO_2 (*liter*)	CO (*liter*)	Hydrocarbons (*liter*)	Water layer (*cc.*)	Oily layer (*cc.*)
1.043	114	147	134	84	..	..	..	..	..
1.028	38	56	119	37	40	5	17	93	133
(1.047)	(47)	(67)	..	..	24	2	2	..	..
1.037	51	82	124	..	44	5	4	94	73
1.034	35	57	125	46	57	7	5	151	116
1.027	42	65	134	50	50	6	10	95	110
1.024	40	69	134	20	49	11	16	174	265
1.043	81	105	113	62	35	1	2	107	35

Decarboxylation. The decarboxylation of organic acids by the application of heat may be expressed by the following equation:

$$R{-}CH_2{-}COOH \longrightarrow R{-}CH_3 + CO_2$$

The two experimental values, volume of CO_2 liberated and decrease in acidity, are related and it is possible to calculate the theoretical value of the former by consideration of the saponification values of the resin before and after running. This has been done and comparison of the two is made in Table XLI.

The critical decarboxylation temperature for white congos appears to be about 300°C. At this temperature the evolution of carbon dioxide becomes considerable (see Figs. 28 and 29). If maintained at 300°C., a steady liberation of gas is initially observed, which after some time begins to diminish rapidly and, before the final drop, again becomes constant for a short period. Once this final drop has been reached, further heating at 300°C. effects no further decarboxylation. However, if the temperature is increased to 350°C., evolution of carbon dioxide begins anew, with the rate increasing rapidly to a maximum and then diminishing continuously thereafter.

Rate of evolution curves of similar shape were obtained from all the

TABLE XL

EVOLUTION OF GAS DURING EXPERIMENT 1.

Time (*min.*)	Temperature °C.	Total Volume		CO_2				CO				Hydrocarbons			
		V (*liter*)	*dV* (*liter*)	Per cent (*liter /hr.*)	*dV* (*liter*)	*V* (*liter*)	*R* (*liter /hr.*)	Per cent	*dV* (*liter*)	*V* (*liter*)	*R* (*liter /hr.*)	Per cent	*dV* (*liter*)	*V* (*liter*)	*R* (*liter /hr.*)
35	190	0													
			2	70	1.4		16.8	0	0		0	30	0.6		7.2
40	192	2				1.4				0				0.6	
			5.2	70	3.7		22.2	0	0		0	30	1.5		9.0
50	244	7.2				5.1				0				2.1	
			9.8	88	86		59.6	2	0.2		1.2	16	1.1		6.6
60	270	17				13.7				0.2				3.3	
			14	88	12.6		75.6	6	0.8		4.8	9	1.2		7.2
70	296	31				26.3				1.0				4.5	
			17	50	8.5		51.0	22	3.7		22.2	27	4.6		25.6
80	315	48				34.8				4.7				9.1	
			14.5	35	5.1		60.0	12	1.7		20.4	49	7.5		90
85	280	62.5				39.9				5.4				16.6	

Volumes are given in liters.
***V* is the total volume evolved up to the time indicated.**
***dV* represents the volume formed during the time interval indicated.**
***R* is the rate of evolution.**

TABLE XLI

COMPARISON OF THEORETICAL WITH ACTUAL VOLUMES OF CO_2 EVOLVED DURING THE RUNNING OF CONGO

Experiment Number	Congo	Volume of CO_2 Formed	
		Calculated	Obtained experimentally
3	White	46	44
4	White	59	58
5	White	55	50
6	White	50	49
7	White	31	35
9	Amber	29	23
11	Brown	35	31
12	Brown	45	49

experiments on white congo. The course of heat treatment had some effect upon the intensity of the reactions, but did not cause any fundamental difference. Rapid heating was found to give very sharp maxima, closely spaced (see curve for experiment 3 in Fig. 30), whereas slower heating produced less definite and more widely spaced maxima (see curves for experiments 6 and 7 in Fig. 30).

Hellinckx concluded that two successive decarboxylations occur in the running of white congo. The first phase is indicated by the first maximum in the rate of evolution curves and occurs at 300°C., being fully developed only at about 350°C.

Previous investigators have shown that congo contains dicarboxylic acids of the general formula $C_{36}H_{58}(COOH)_2$. According to Hellinckx, an explanation of the two-stage decarboxylation may possibly be found in the assumption that the two COOH groups have different stabilities and do not break down at the same time or temperature. Heat treatment could give rise to two successive decarboxylations:

(1) $C_{36}H_{58}(COOH)_2 \longrightarrow C_{36}H_{59}COOH + CO_2$
(2) $C_{36}H_{59}COOH \longrightarrow C_{36}H_{60} + CO_2$

The greater stability of the monobasic acid formed may be the important factor.

It was found necessary to use 350°C. as a running temperature for

brown congos rather than the lower temperatures which were satisfactory for the white variety. For this reason, although two maxima again appeared in the rate of carbon dioxide evolution curves (Fig. 31), they were spaced more closely. The output of gas did not drop off between the points of maxima so sharply as it did with the white copals. Hellinckx believes that at the temperatures used in the running of the brown congo, part of the resin, which had undergone the first decarboxylation and was at the appropriate temperature (350°C.), passed through the second decarboxylation before the first was complete for

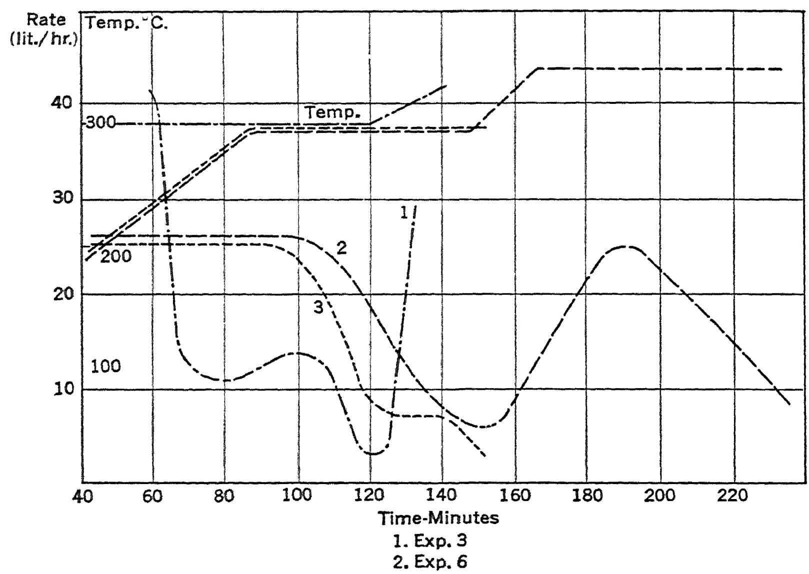


FIG. 30. Rate of evolution of CO_2-white congo. (Hellinckx)

the entire mass. It appears that the temperature required for the first phase of decarboxylation is higher for brown than for white congos. Age differences may be a factor. Amber grades of congo were found to behave similarly to the white variety.

Cracking. According to Hellinckx, the formation during running of products having molecular weights considerably below that of the parent constituents can be explained by cracking, i.e., the breaking down of complex organic molecules under the influence of heat into a number of simpler compounds.

Upon analysis, the aqueous layer from the distillate was found to

contain water, acids, aldehydes, and ketones. Formic and acetic acids as well as traces of succinic acid were identified.

From the oily layer, two compounds were isolated. The first corresponded to a monocyclic terpene, laevo-rotatory limonene, the other to a bicyclic sesquiterpene with two pairs of double bonds, not previ-

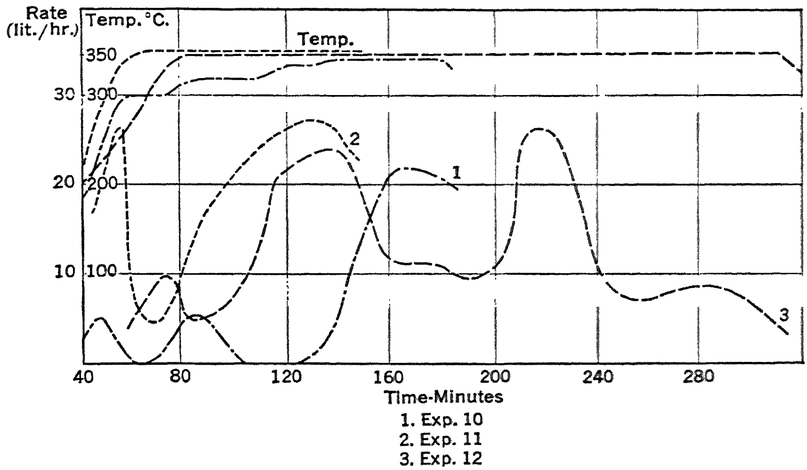
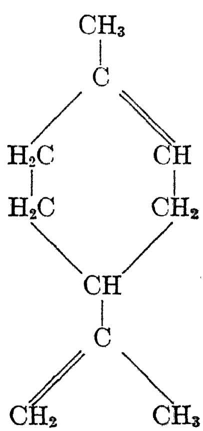
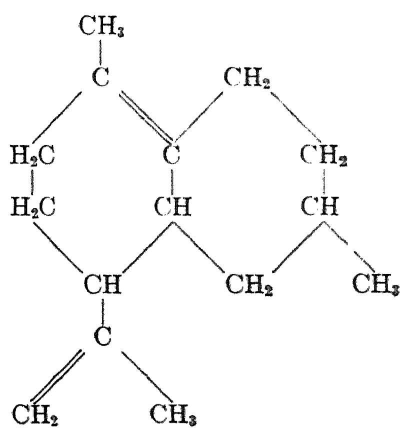


FIG. 31. Rate of evolution of CO_2-brown congo. (Hellinckx)

ously described in the literature, but assigned by Hellinckx the name congolene.



Limonene



Congolene[16]

[16] Probable formula (after Hellinckx).

The original resin contains limonene,[17] but Hellinckx holds that it is unlikely that congolene is also present. Congolene may be a product of cracking. As congolene decomposes upon heating to give chiefly limonene, it is possible that part of the latter is formed in this manner during the running operation. Other less well-defined fractions were also obtained. Some of these were of an acidic nature.

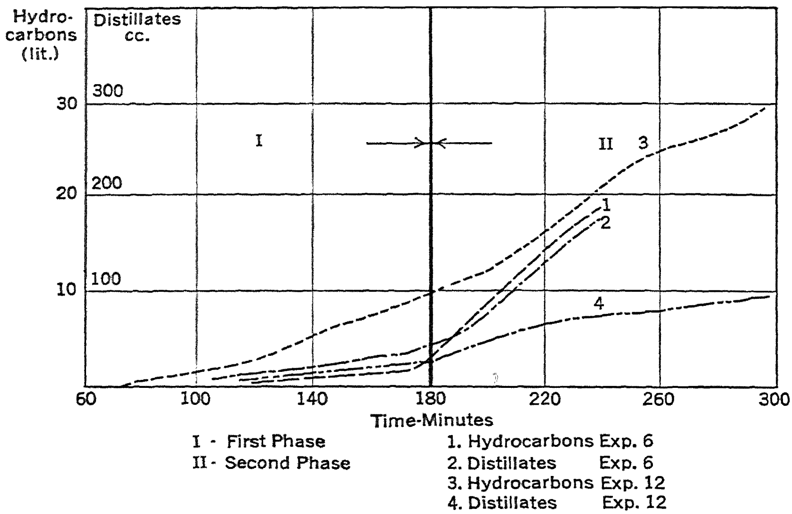


FIG. 32. Effect of temperature on cracking. (Hellinckx)

Little cracking was found to occur at about 300°C. since the amounts of gaseous hydrocarbons and oily distillates formed were very small. Upon elevation to 350°C., however, the effects of cracking became considerable, and violent evolution of gaseous hydrocarbons, together with the formation of large quantities of distillate, indicated rapid decomposition of the resin. Figure 32 shows the effect of temperature on cracking.

With the white copals, therefore, cracking is a secondary reaction of little importance during the first phase of running, but if the temperature be raised to 350°C., cracking rapidly increases and becomes the predominating reaction during the second phase.

Because the two phases of decarboxylation of brown congo occur at the same temperature, 350°C., it would be expected that cracking should be equally developed in each phase. However, the violence of the

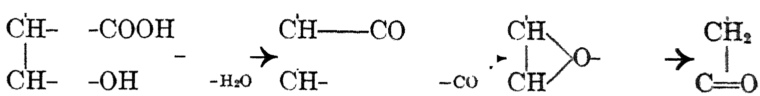
[17] It is this hydrocarbon which is responsible for the pleasant odor given off when congo is ground.

first decarboxylation appears to exert a retarding influence on its development. This can be seen from experiment 12 in Fig. 31.

Reactions Responsible for the Liberation of Carbon Monoxide. Hellinckx noted the regular liberation of carbon monoxide. The volume evolved was small while the resin was being run at moderate temperatures, but increased rapidly with stronger heating. Evolution of carbon monoxide, negligible during the first phase of running, becomes considerable during the second.

The acetyl value of the resin decreased as the volume of carbon monoxide evolved increased. This was true for all varieties of congo. As the acetyl value of a substance indicates the presence of hydroxy acids,[18] Hellinckx attributed the generation of carbon monoxide to the instability of these when heated. It is known that hydroxy acids frequently yield carbon monoxide upon heating. The reaction takes place in two stages: first, internal anhydrides are formed by the loss of one molecule of water from each molecule of hydroxy acid; in the second, these internal anhydrides decompose with the liberation of carbon monoxide.

In the case of the hydroxy acids of congo, the reaction is somewhat different, due to the aromatic nature of the resin. Hellinckx assumed that the carboxyl and hydroxyl groups were attached to two neighboring carbon atoms within the molecule.



In the first stage water is lost and the anhydride is formed; in the second stage carbon monoxide separates. The reaction is probably completed by an internal change to a more stable form. The formation of anhydrides was indicated by a fall in acetyl value, due to the disappearance of the hydroxyl groups upon which this value depends.

Mantell, Allen, and Sprinkel[19] studied the running of congo No. 11 to determine the time, temperature, and other conditions necessary to make it oil soluble. The methods of running were varied widely to show their effect on the process itself and on the properties of the run resin.

One-gallon, heavy-walled, chrome-nickel kettles were used (6½ in.

[18] The presence of these in congo had already been proved by A. Tschirch and A. Engel, *Arch. Pharm.*, **246**, 293 (1908).

[19] C. L. Mantell, C. H. Allen, and K. M. Sprinkel, *Paint, Oil Chem. Rev.*, No 17, p. 9 (1936).

in diameter and 9 in. deep). The kettles were fitted with removable covers having a drip ring to return the condensate to the kettle without running down its overheated sides. In the cover were thermometer and funnel holes and a larger opening for stirring which had a closely fitting, easily removable lid.

Heating, cooling, and other details of the process were carried out as shown by experience to give results closely duplicating factory conditions.

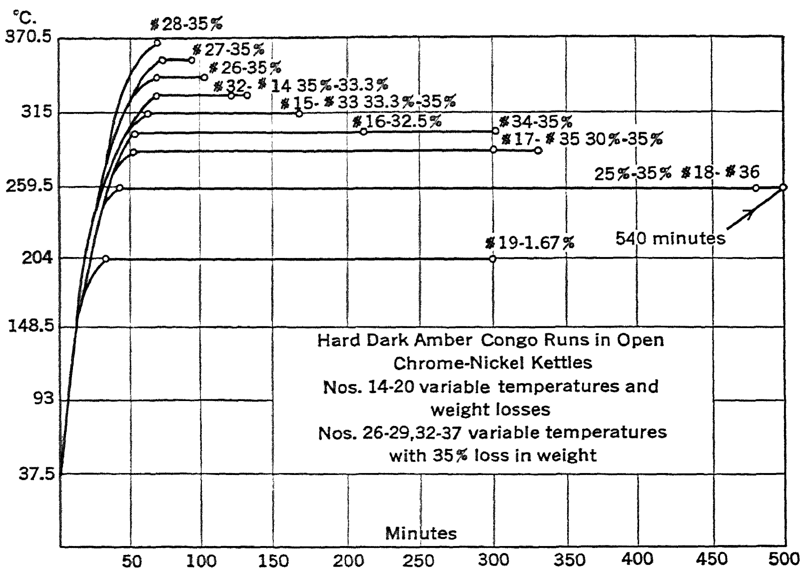


FIG. 33.

Six-hundred-gram lots were heated to raise the temperature approximately 5.5°C. (10°F.) per minute until the desired maximum temperature was reached.

Four series of run congos were made in which the maximum temperatures varied from 205 to 271°C. Two runs were performed in an open kettle and two in a closed kettle. The former consisted of runs with variable losses in weight and with the maximum temperature held until the loss was 35 per cent. The latter included runs with variable losses and with the maximum temperature held to a 20 per cent loss. Time and temperature curves for the runs are given in Figs. 33 and 34.

Open-Kettle Runs—Variable Weight Losses. The open-kettle series, No. 14 to No. 19, were run at temperatures from 205°C. (400°F.)

to 330°C. (625°F.). The constant weight-loss runs, No. 28 to No. 36, at 344°C. (650°F.) to 370°C. (700°F.) have been grouped with them to complete the temperature scale. The early portions of the curves coincide because of the uniform initial heating rate.

At 205°C. (400°F.) congo is merely softened a little where it touches the bottom of the kettle. After 1.7 per cent loss it came to constant weight.

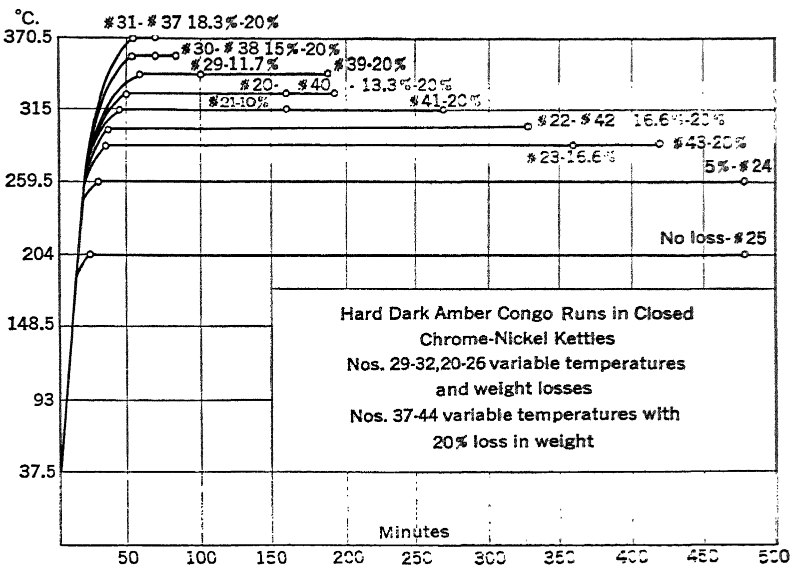


Fig. 34.

After 2½ hours at 260°C. (500°F.), most of the resin had become a foamy, waxy mass. During the next 5 hours it became first a heavy-bodied liquid and finally a liquid similar to medium boiled linseed oil. It still had some spongy lumps floating in it. Congo run at this temperature was not completely oil soluble even after 8 hours of cooking.

Four hours at 288°C. (550°F.) changed all the resin to a thin liquid, similar to hot oil, which gave a clean drip from the paddle. At this temperature the resin was completely run, but the heating time was long.

Runs at 302°C. (575°F.), 315°C (600°F.), and 330°C. (625°F.) required 160, 105, and 65 minutes respectively to completely run the resin.

The weight losses for this series varied from 25 per cent at 260°C. (500°F.) to 33.3 per cent at 330°C. (625°F.).

Open-Kettle Runs—35 per Cent Loss in Weight. In this series the maximum temperature varied from 260 to 371°C. (500-700°F.). All runs but that at 260°C. produced oil-soluble resin. The times at maximum temperature varied from 0 at 371°C. (700°F.) to 6½ hours at 288°C. (550°F.).

Closed-Kettle Runs—Variable Loss in Weight. These runs were similar to those in the open-kettle series. At 205°C. there was no loss in weight, and after 8 hours the resin was almost entirely unchanged. After 7 hours at 260°C. (500°F.) with a 5 per cent weight loss, a spongy, waxy mass remained which was much less nearly run than the open-kettle run with a 25 per cent loss at the same temperature.

Runs Nos. 20-23, inclusive, at 280 to 330°C. (536-626°F.) with only 10 to 16.6 per cent loss in weight gave run resins with a clean drip from the paddle, but contained some spongy pieces of incompletely run resin.

The congos run at 344, 357, and 371°C. (651, 675, and 700°F.) produced resins of complete oil solubility. Run No. 29 (at 344°C.) with only 11.7 per cent loss was exceptional.

Closed-Kettle Runs—20 per Cent Loss in Weight. The maximum temperatures in these runs varied from 260 to 371°C. (500 to 700°F.) and the time at temperature from 15 minutes at 371°C. to 7 hours at 260°C. There were a few pieces of incompletely run resin at 260°C. All the other runs gave a clean drip and oil-soluble resins.

The physical and chemical properties of the run resins obtained in the investigation are given in Tables XLII and XLIII, together with their solubilities and viscosities in five representative solvents.

The greater hardness of the run resins from open kettles is indicated by their higher softening and melting points as compared with those from closed kettles.

The solubilities and the viscosities of the run-congo solutions were determined in a manner described previously in this volume. The solubility tests show conclusively the excellent solubility of the run congos in the solvents used. Failure of a run-congo sample, therefore, to dissolve in any of these solvents may be evidence of a poor running procedure.

In Figs. 35, 36, 37, and 38 the solution viscosities of the run resins have been plotted against maximum temperature for each of the four series studied. In all four, the curves lie in the following order of increasing viscosity: butyl acetate, toluol, hydrogenated naphtha, n-butanol, and mineral spirits. In each of the four series of runs the majority of the viscosities decrease as the temperature at which the

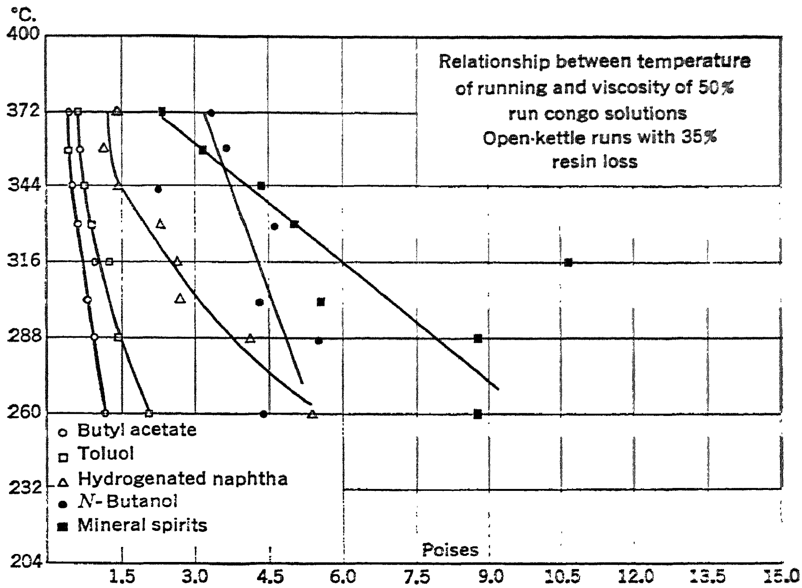

°C.
400
372
344
316
288
260
232
204
Relationship between temperature of running and viscosity of 50% run congo solutions Open-kettle runs with 35% resin loss
o Butyl acetate
□ Toluol
△ Hydrogenated naphtha
● N-Butanol
■ Mineral spirits
Poises
1.5
3.0
4.5
6.0
7.5
9.0
10.5
12.0
13.5
15.0

FIG. 35.

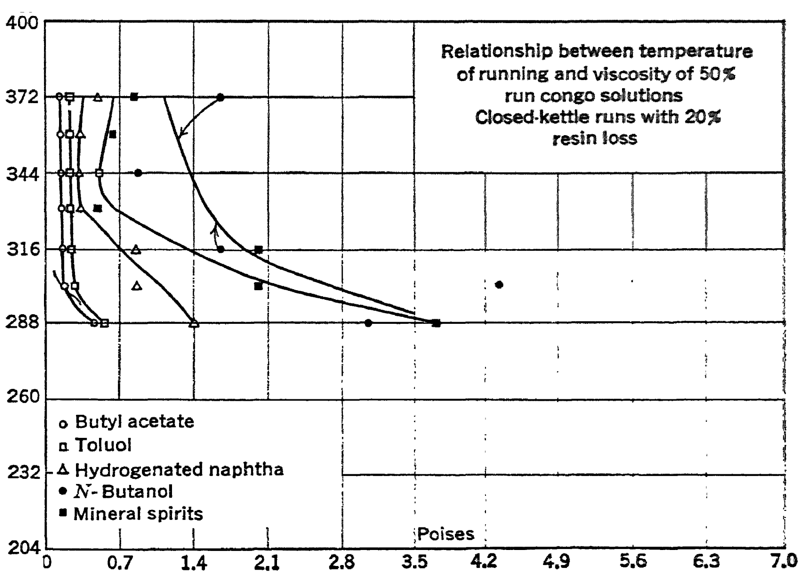

400
372
344
316
288
260
232
204
Relationship between temperature of running and viscosity of 50% run congo solutions Closed-kettle runs with 20% resin loss
o Butyl acetate
□ Toluol
△ Hydrogenated naphtha
● N-Butanol
■ Mineral spirits
Poises
0
0.7
1.4
2.1
2.8
3.5
4.2
4.9
5.6
6.3
7.0

FIG. 36.

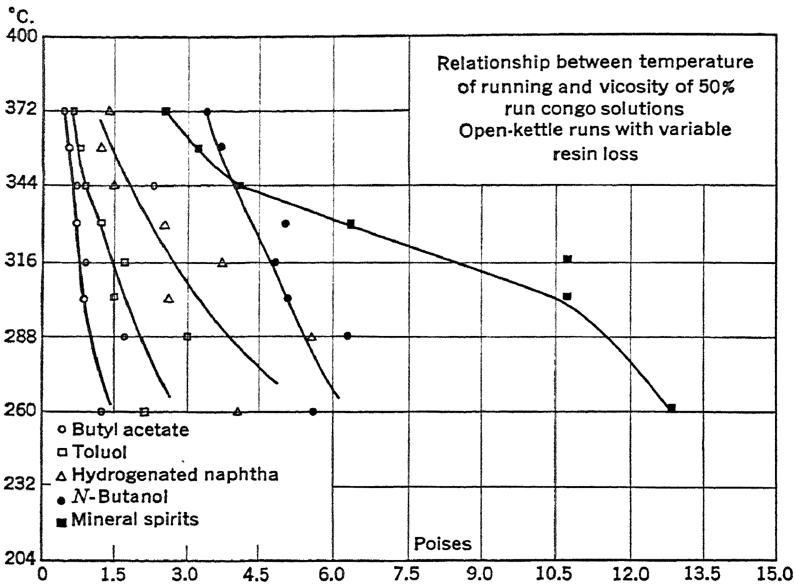

°C.
400
372
344
316
288
260
232
204
Relationship between temperature of running and vicosity of 50% run congo solutions Open-kettle runs with variable resin loss
o Butyl acetate
□ Toluol
△ Hydrogenated naphtha
● N-Butanol
■ Mineral spirits
Poises
0
1.5
3.0
4.5
6.0
7.5
9.0
10.5
12.0
13.5
15.0

Fig. 37.

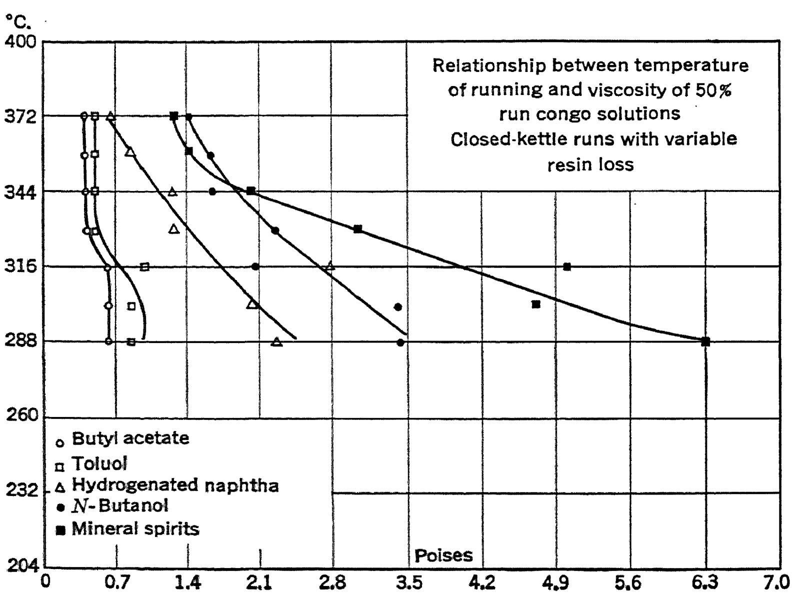

°C.
400
372
344
316
288
260
232
204
Relationship between temperature of running and viscosity of 50% run congo solutions Closed-kettle runs with variable resin loss
o Butyl acetate
□ Toluol
△ Hydrogenated naphtha
● N-Butanol
■ Mineral spirits
Poises
0
0.7
1.4
2.1
2.8
3.5
4.2
4.9
5.6
6.3
7.0

Fig. 38.

resins were run increases. If viscosity be considered an index of solubility, higher temperatures produce more soluble run resins.

Properties of Run Resins. Natural resins are run primarily to convert them to an oil-soluble form, although frequently, the product may be used in a spirit-base vehicle. Occasionally, resins are processed only to a degree sufficient to render them soluble in organic solvents. The heating period is shorter and the temperatures used are below those necessary to secure complete oil solubility. Resins processed in this manner are sometimes called "fused" resins, but the designation is not definite, as the term "fused" is also applied to completely run resins.

The sharply drawn lines dividing the different natural resins into definite solubility types disappear almost completely after the resin has been thermally processed. For example, all run resins, regardless of their original solubility characteristics, are soluble in petroleum solvents, coal-tar solvents, turpentine and other terpenic solvents, ethers, and the higher esters and alcohols. All are insoluble in methyl, ethyl, and isopropyl alcohols and their esters, whereas most of them are completely soluble in butyl alcohol.

Thermal processing always extends the range of solvents for any resin so treated, but in certain instances may convert the resin to a form insoluble in one of its former solvents. A notable example of this is the loss of alcohol solubility by manilas and kauris in their run modifications.

Solubility and viscosity determinations on run resins have been performed in the manner previously described for unrun resins. Tables XLIV, XLV, and XLVI list the solubilities and viscosities of run resins in petroleum and other organic solvents.

Effect of Running on the Physical and Chemical Constants of Natural Resins. Because of the severe thermal treatment involved, running is always attended by a change in the physical and chemical constants of the resins. Figures are given in Table XLVII for the constants of representative run resins. The constants are merely typical, as they are determined by the method of processing and the weight loss suffered. The constants given in Table XLVII were compared with those of the original resins and the changes listed in Table XLVIII.

Though the results are irregular, the data show well-defined trends such as the lowering of acid, saponification, and iodine numbers. The effect on softening and melting point values was not regular, the damars and manilas appearing to increase, and the east indias, kauris, and congos appearing to decrease. The decrease in acid number with greater weight loss is readily apparent in Table XLIX.

TABLE XLII

Physical and Chemical Properties of Congos Run in Open Kettles

R. R. No.	Max. Temp. of Run °C.	Per Cent Resin Loss	Softening Pt. °C.	Melting Pt. °C.	Direct Acid No.	Indirect Acid No.	Solubilities and Viscosities (Solutions 1:1 by Weight)														
							Varnolene			Hydrogenated Naphtha			Toluol			Butyl Acetate			N-Butanol		
							Solubility	Viscosity		Solubility	Viscosity		Solubility	Viscosity		Solubility	Viscosity		Solubility	Viscosity	
								G.-H.*	Poises		G.-H.*	Poises		G.-H.*	Poises		G.-H.*	Poises		G.-H.*	Poises
Hard dark amber congo run to a clean drip—variable loss in weight																					
HDAC			100	200†	70.1†	111.7	I			Sw			Sw			Sw			Sw		
CRC			95	140	76.0	83.7	PS-Sw			S	O	3.70	S	R	4.70	S	C	0.85	S	K	2.75
19	205	1.7	108	185†	76.6†	106.0	I-PSw			Sw			Sw			Sw			Sw		
18	260	25.0	104	148	75.4	79.7	S	X	12.00	S	P	4.00	S	H	2.00	S	E	1.25	S	T	5.50
17	288	30.0	92	150	78.4	83.6	PS-Sw			S	T	5.50	S	L	3.00	S	G	1.65	S	U	6.27
16	302	32.5	106	148	69.4	75.2	S	W	10.70	S	J	2.50	S	F	1.40	S	C	0.85	S	S	5.00
15	315	33.3	110	150	70.7	75.7	S	W	10.70	S	O	3.70	S	G	1.65	S	C	0.85	S	R	4.70
14	330	33.3	94	148	75.4	80.8	S	U	6.27	S	J	2.50	S	E	1.25	S	B	0.65	S	S	5.00
Hard dark amber congo run to a constant loss in weight																					
28	371	35	102	145	57.7	64.0	S	J	2.50	S	F	1.40	S	A	0.50	S	A	0.50	S	N	3.40
27	357	35	100	145	60.6	66.2	S	M	3.20	S	E	1.25	S	B	0.65	S	A	0.50	S	O	3.70
26	344	35	108	154	70.7	75.2	S	P	4.00	S	F	1.40	S	B	0.65	S	B	0.65	S	I	2.25
32	330	35	110	158	67.1	72.9	S	S	5.00	S	J	2.50	S	C	0.85	S	B	0.65	S	R	4.70
33	315	35	110	155	67.1	72.9	S	W	10.70	S	L	3.00	S	E	1.25	S	D	1.00	S	Q	4.35
34	302	35	105	160	59.4	66.2	S	T	5.50	S	K	2.75	S	C	0.85	S	C	0.85	S	Q	4.35
35	288	35	105	166	68.8	74.0	S	V	8.84	S	P	4.00	S	F	1.40	S	D	1.00	S	T	5.50
36	260	35	115	170	65.3	70.2	S	V	8.84	S	T	5.50	S	H	2.00	S	E	1.25	S	Q	4.35

* Letters correspond to Gardner-Holdt viscosity tubes.
† Average of several determinations.
Runs 26, 27, 28 complete the temperature range for each series.
HDAC Hard dark amber congo—not run.
CRC Commercial run congo.

Abbreviations: S, soluble
PS, partly soluble
Sw, swelled
I, insoluble

TABLE XLIII

PHYSICAL AND CHEMICAL PROPERTIES OF CONGOS RUN IN CLOSED KETTLES

R. R. No.	Max. Temp. of Run °C.	Per Cent Resin Loss	Softening Pt. °C.	Melting Pt. °C	Direct Acid No.	Indirect Acid No.	Solubilities and Viscosities (Solutions 1:1 by Weight)														
							Varnolene			Hydrogenated Naphtha			Toluol			Butyl Acetate			N-Butanol		
							Solubility	Viscosity G.-H.*	Viscosity Poises	Solubility	Viscosity G.-H.*	Viscosity Poises	Solubility	Viscosity G.-H.*	Viscosity Poises	Solubility	Viscosity G.-H.*	Viscosity Poises	Solubility	Viscosity G.-H.*	Viscosity Poises
Hard dark amber congo run to a clean drip—variable loss in weight																					
25	205		110	215†	67.7†	114.0	I-PSw			Sw			Sw			Sw			Sw		
24	260	5.0	110	220†	67.7†	88.7	PS-Sw			Sw			Sw			Sw			Sw		
23	288	16.6	102	148	73.6	76.8	S	U	6.27	S	I	2.25	S	C	0.85	S	B	0.65	S	N	3.40
22	302	16.6	102	145	70.7	75.7	S	R	4.70	S	H	2.00	S	C	0.85	S	B	0.65	S	N	3.40
21	315	10.0	94	135	80.8	86.9	S	S	5.00	S	K	2.75	S	D	1.00	S	B	0.65	S	H	2.00
20	330	13.3	85	128	64.8	68.4	S	L	3.00	S	E	1.25	S	A	0.50	S	A –	0.50	S	I	2.25
29	344	11.7	85	126	67.7	78.0	S	H	2.00	S	E	1.25	S	A	0.50	S	A –	0.50	S	G	1.65
30	357	15.0	85	128	63.0	79.0	S	F	1.40	S	C	0.85	S	A	0.50	S	A –	0.50	S	G	1.65
31	371	18.3	80	115	61.1	71.8	S	E	1.25	S	B	0.65	S	A	0.50	S	A –	0.50	S	F	1.40
Hard dark amber congo run to a constant loss in weight																					
43	288	20	95	143	65.3	70.2	S	O	3.70	S	F	1.40	S	A	0.50	S	A	0.50	S	L	3.00
42	302	20	85	140	55.8	61.7	S	H	2.00	S	C	0.85	S	A –	0.50	S	A –	0.50	S	Q	4.35
41	315	20	75	128	68.8	74.0	S	H	2.00	S	C	0.85	S	A –	0.50	S	A –	0.50	S	G	1.65
40	330	20	70	108	32.6	47.2	S	A	0.50	S	‡A –	0.50	S	A –	0.50	S	A –	0.50	PS-Sw		
39	344	20	70	104	42.8	51.6	S	A	0.50	S	A –	0.50	S	A –	0.50	S	A –	0.50	S	C	0.85
38	357	20	75	110	46.3	53.8	S	B	0.65	S	A –	0.50	S	A –	0.50	S	A –	0.50	PS-Sw		
37	371	20	85	110	55.2	66.2	S	C	0.85	S	A	0.50	S	A	0.50	S	A –	0.50	S	G	1.65

* Letters correspond to Gardner-Holdt viscosity tubes.
† Average of several determinations.
‡ Gardner-Holdt viscosity A – is less than 0.50 poise.

TABLE XLIV. SOLUBILITY

Solvent	Batavia Damar A D	Batavia Damar Standard A E	Batu East India Nubs and Chips	Black East India Bold Scraped	Boea Hard Bold Amber	Congo No. 1 Water-white	Congo No. 4 Pale Bold Straw	Congo No. 11 H. D. Amber Bold
Acetone	Soluble	Soluble	Partly Sol.	Sl. Sol.	Sl. Sol.	Sl. Sol.	Sl. Sol.	Insol.
Amyl acetate	"	"	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
Amyl alcohol, secondary	"	"	"	"	"	"	"	"
Amyl chloride	"	"	"	"	"	"	"	"
Aniline	"	Swelled	Swelled	Insol.	"	"	"	"
Ansol	Sl. Sol.	Sl. Sol.	Sl. Sol.	Sl. Sol.	Sl. Sol. Sed	Insol.	Insol.	Insol.
Benzol	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
Benzyl alcohol	"	Swelled	Swelled	Swelled	"	" Sed	"	"
Butyl acetate	"	Soluble	Soluble	Soluble	"	"	"	"
Butyl alcohol, normal	"	"	Swelled	Sl. Sol.	"	" Sed	"	"
Butyl Carbitol	"	" Sed	"	Swelled	"	"	"	"
Butyl ether	"	"	Soluble	Soluble	"	"	"	"
Butyl lactate	"	"	Swelled	Sl. Sol.	"	"	"	"
Carbon tetrachloride	Soluble	Soluble	G.L.	Soluble	Swelled	Soluble	Soluble	Soluble
Cellosolve	"	"	Swelled	Insol.	Soluble	" Sed	"	" Sed
Chlorbenzol	"	"	Soluble	Soluble	"	"	"	"
Diacetone alcohol	Sl. Sol.	Sl. Sol.	Swelled	Insol.	" Sed	Insol.	Insol.	Insol.
Dichloroethyl ether	Soluble	Soluble	"	Swelled	Swelled	Soluble	Soluble	Soluble
Diethyl carbonate	"	"	Soluble	Soluble	Soluble	"	"	"
Dimethyl phthalate	Swelled	Swelled	Insol.	Swelled	Insol.	Swelled	Swelled	Swelled
Dioxane	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
Dipentene	"	"	"	"	"	"	"	"
Ethyl abietate	Swelled	Swelled	G.L.	Swelled	Swelled	Swelled	Swelled	Swelled
Ethyl acetate	Soluble	Soluble	Soluble	Sl. Sol.	Soluble	Soluble	Soluble	Soluble
Ethyl ether	"	"	"	Soluble	"	"	"	"
Hercosol 80	"	"	"	"	"	"	"	"
Hexalin	"	Lgly. Sol.	"	"	Lgly. Sol.	Lgly. Sol.	Lgly. Sol.	Lgly. Sol.
Isopropyl alcohol	Sl. Sol.	Insol.	Insol.	Insol.	Sl. Sol.	Insol.	Insol.	Insol.
Methyl acetone	Soluble	Soluble	Partly Sol.	Sl. Sol.	Soluble	Lgly. Sol.	Sl. Sol.	Sl. Sol.
Methyl alcohol	Swelled	Insol.	Insol.	Insol.	Insol.	Insol.	Insol.	Insol.
Methyl salicylate	Soluble	Soluble	Soluble	Sl. Sol.	Soluble	Soluble	Soluble	Soluble
Nitrobenzol	"	"	Swelled	Swelled	"	"	"	"
Octyl acetate	"	"	Soluble	Soluble	"	"	"	"
Petroleum naphtha				see special	chart			
Phenol 60°C.	Soluble	Soluble	Soluble	Partly Sol.	Soluble	Soluble	Soluble	Soluble
25°C.	"	"	"	Soluble	"	" Sed	" Sed	"
Shellacol	Swelled	Insol.	Insol.	Insol.	Insol.	Insol.	Insol.	Insol.
Solox	"	"	"	"	"	"	"	"
Terpineol	Soluble	Soluble	Soluble	Soluble	Partly Sol.	Lgly. Sol.	Partly Sol.	Lgly Sol.
Tetrachloroethane	"	"	Lgly. Sol.	"	Swelled	Soluble	Soluble	Soluble
Tetralin	"	"	Soluble	"	Soluble	"	"	"
Toluol	"	"	"	"	"	"	"	"
Tricresyl phosphate	Swelled	Swelled	Swelled	Insol.	Swelled	Swelled	Swelled	Swelled
Turpentine	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
Xylol	"	"	"	"	"	"	"	"

* All determinations made with 100 g. of resin and 100 g. of solvent.

Soluble, 90 to 100% of resin dissolved

Largely soluble, 50 to 90% of resin dissolved

Partly soluble, 25 to 50% of resin dissolved

Slightly soluble, 5 to 25% of resin dissolved

Insoluble, resin unaffected by solvent

of Run Natural Resins*

No. 21 Selected Nubs	East India Macassar Nubs	East India Singapore Nubs	Kauri Pale No. 2	Kauri Brown No. 2	Manila Loba C	Manila CBB	Manila DBB	Philippine Manila Bold Pale Chips	Pontianak Bold Scraped
Insol.	Swelled	Sl. Sol.	Swelled	Sl. Sol.	Soluble Sed	Lgly. Sol.	Sl. Sol.	Lgly. Sol.	Sl. Sol.
Soluble	Soluble	Soluble	Soluble	Soluble	”	Soluble	Soluble	Soluble	Soluble
”	”	Sl. Sol.	”	”	”	”	”	”	”
”	”	Soluble	”	”	”	”	”	”	”
”	Insol.	Insol.	”	”	”	”	”	”	”
Insol.	Sl. Sol.	”	Swelled	Swelled	Sl. Sol.	Sl. Sol.	Sl. Sol.	Swelled	Sl. Sol.
Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
”	Swelled	Insol.	”	”	”	”	”	”	”
”	Soluble	Soluble	”	”	”	”	”	”	”
”	Sl. Sol.	Swelled	Sl. Sol.	Sl. Sol.	”	”	”	”	”
”	Swelled	Insol.	Soluble	Soluble	”	”	”	”	”
”	Soluble	Soluble	”	”	”	”	”	”	”
”	Sl. Sol.	Swelled	”	”	”	”	”	”	”
Soluble	Soluble	Swelled	Soluble	Soluble	Swelled	Soluble	Soluble	Soluble	Swelled
”	Sl. Sol.	Insol.	Sl. Sol.	Sl. Sol.	Soluble	”	”	”	Soluble
”	Soluble	Soluble	Soluble	Soluble	”	”	”	”	”
Insol.	Sl. Sol.	Swelled	Sl. Sol.	Sl. Sol.	”	” Sed	Sl. Sol.	Sl. Sol.	”
Soluble	Swelled	”	Soluble	Soluble	”	”	Soluble	Soluble	”
”	Soluble	Partly Sol.	”	”	”	”	”	”	”
Swelled	Insol.	Insol.	Swelled	Swelled	Swelled	Insol.	Swelled	Swelled	Insol.
Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
”	”	”	”	”	”	”	”	”	”
Swelled	Swelled	Swelled	Sl. Sol.	Swelled	Swelled	Insol.	Swelled	Swelled	G.L.
Soluble	Lgly. Sol.	Partly Sol.	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
”	Soluble	Soluble	”	”	”	”	”	”	”
”	”	”	”	”	”	”	”	”	”
”	”	Swelled	Partly Sol.	”	Partly Sol.	Lgly. Sol.	”	”	Partly Sol.
Insol.	Sl. Sol.	”	Swelled	Swelled	Insol.	Sl. Sol.	Sl. Sol.	Swelled	Sl. Sol.
Soluble	Swelled	Sl. Sol.	”	”	Soluble Sed	Lgly. Sol.	”	Lgly. Sol.	Soluble
Insol.	Insol.	Insol.	”	Insol.	Insol.	Insol.	Swelled	Swelled	Insol.
Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
”	Swelled	Swelled	”	”	”	”	”	”	”
”	Soluble	Soluble	”	”	”	”	”	”	”
Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
”	”	”	G.L.	”	” Sed	” Sed	” Sed	” Sed	”
Insol.	Insol.	Insol.	Swelled	Swelled	Insol.	Insol.	Swelled	Swelled	Insol.
”	”	”	”	”	”	”	”	”	”
Lgly. Sol.	Lgly. Sol.	Sl. Sol.	Lgly. Sol.	Soluble	Partly Sol.	Partly Sol.	Soluble	Soluble	Sl. Sol.
Soluble	Soluble	Swelled	Soluble	”	Soluble	Soluble	”	”	Swelled
”	”	Soluble	”	”	”	”	”	”	Soluble
”	”	”	”	”	”	”	”	”	”
Swelled	Insol.	Insol.	Swelled	Swelled	Swelled	Swelled	Swelled	Swelled	Swelled
Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
”	”	”	”	”	”	”	”	”	”

Abbreviations: Insol., insoluble; Sol., soluble; Lgly. Sol., largely soluble; Sl. Sol., slightly soluble.
Swelled resin so affected by solvent; G.L. gelatinous liquid resulted.
T.V.G. transparent viscous gel formed. Sed a sediment formed in the solution on standing.

TABLE XLV. Solubility of Run Natural
for Characteristics

(See sepa

	Trade Name	Batavia Damar A D	Batavia Damar Standard A E	Batu East India Nubs and Chips	Black East India Bold Scraped	Boea Manila Hard Bold Amber	Congo No. 1 Water-White Trans-parent	Congo No. 4 Pale Bold Straw	Congo No. 11 Hard Dark Amber Bold
1	D. C. Naphtha	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
2	Varnolene	"	"	"	"	"	"	"	"
3	Kerosene	"	"	"	"	"	"	"	"
4	Torch Oil	"	"	"	"	Sl. Sol.	"	Partly Sol.	"
5	Solvent Naphtha No. 54	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
6	Solvent Naphtha No. 55	"	"	"	"	"	"	"	"
7	V. M. P. Naphtha	"	"	"	"	"	"	"	"
8	Varsol No. 2	"	"	"	"	"	"	"	"
9	Solvesso No. 1	"	"	"	"	"	"	"	"
10	Solvesso No. 2	"	"	"	"	"	"	"	"
11	Solvesso No. 3	"	"	"	"	"	"	"	"
12	Solvesso No. 4	"	"	"	"	"	"	"	"
13	Petrobenzol	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
14	Troluoil	"	"	"	"	"	"	"	"
15	Apcothinner	"	"	"	"	"	"	"	"
16	Apco 125	"	"	"	"	"	"	"	"
17	Apco B-75	"	"	"	"	"	"	"	"
18	Sunoco Spirits	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
19	Special Sunoco Spirits	"	"	"	"	"	"	"	"
20	Sinclair Rubber Solvent	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
21	Sinclair Naphthol	"	"	"	"	"	"	"	"
22	Sinclair VMP Naphtha	"	"	"	"	"	"	"	"
23	Sinclair Solvent	"	"	"	"	"	"	"	"
24	Sinclair Odorless Insecticide base	"	"	"	"	"	"	"	"

* All determinations made with 100 g. of resin and 100 g. of solvent.
Abbreviations: Sol., soluble; Lgly. Sol., largely soluble; Sl. Sol., slightly soluble.

Although running reduces the acid value of copals, this reduction is not usually carried far enough to yield a resin completely non-reactive towards basic pigments. According to Hellinckx,[20] the reactivity is due to insufficient decarboxylation of the dibasic acids.

A study has been made on the properties of congo run to varying weight losses. The resins were obtained by heating 400 grams of congo No. 11 in a 2-liter distilling flask. The flask was heated in a hot air bath. The fumes evolved were passed through a water-cooled condenser and collected. Heating was continued until the desired weight of distillate had been driven off. The loss in weight of the run resin was obtained from its weight in the distilling flask before and after heating.

[20] L. Hellinckx, "Pyrocopal Reactivity," *Paint Manuf.* 9, No. 9, 280-3 (1939).

RESINS IN VARIOUS PETROLEUM NAPHTHAS
OF SOLVENTS*

rate chart)

Congo No. 21 Selected Nubs Ordinary	East India Macassar Nubs	East India Singapore Nubs	Kauri Pale No. 2	Kauri Brown No. 2	Manila Loba C	Manila CBB	Manila DBB	Philippine Manila Bold Pale Chips	Pontianak Bold Scraped
Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Lgly. Sol.
"	"	"	"	"	"	"	"	"	Soluble
"	"	"	"	"	"	"	"	"	Lgly. Sol.
Lgly. Sol.	"	Lgly. Sol.	Lgly. Sol.	"	Partly Sol.	"	"	"	Partly Sol.
Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Lgly. Sol.
"	"	"	"	"	"	"	"	"	"
"	"	"	"	"	"	"	"	"	"
"	"	"	"	"	"	"	"	"	"
"	"	"	"	"	"	"	"	"	Soluble
"	"	"	"	"	"	"	"	"	"
"	"	"	"	"	"	"	"	"	"
"	"	"	"	"	"	"	"	"	Lgly. Sol.
Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	"
"	"	"	"	"	"	"	"	"	"
"	"	"	"	"	"	"	"	"	Partly Sol.
"	"	"	"	"	"	"	"	"	Lgly. Sol.
"	"	"	"	"	"	"	"	"	Soluble
Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	"
"	"	"	"	"	"	"	"	"	"
Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Lgly. Sol.
"	"	"	"	"	"	"	"	"	"
"	"	"	"	"	"	"	"	"	"
"	"	"	"	"	"	"	"	"	Soluble
"	"	"	"	"	"	"	"	"	Lgly. Sol.

Soluble 90 to 100% of resin dissolved **Largely Soluble** 50 to 90% of resin dissolved
Partly Soluble 25 to 50% of resin dissolved **Slightly Soluble** 5 to 25% of resin dissolved

As good cooling was provided, the loss in weight in excess of the weight of the distillate collected may be considered to be due to the evolution of gases formed by the decomposition of the resin. For those runs with appreciable weight losses, the time of distillation was kept as near constant as possible.

The data for this investigation are given in Table L.

Except for numbers 5 and 8, the softening and melting points show a regular lowering as the running loss increases. Similarly, the direct and indirect acid numbers decrease with increasing weight loss.

Under the conditions which prevailed during the experimental running, a certain amount of refluxing was encountered. This was caused by the condensation of copal oil on the neck of the flask. The continu-

TABLE XLVI. Viscosities of Run Resins

		Batavia Damar A, D		Batavia Damar Standard A, E		Batu East India Nubs and Chips		Black East India Bold Scraped		Boea Hard Bold Amber		Congo					
												No. 1 Water-White Transparent		No. 4 Pale Bold Straw		No. 11 Hard Dark Amber Bold	
		Viscosity	Poise	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise
1	D. C. Naphtha	A	0.50	A	0.50	A	0.50	A	0.50	J	2.50	A	0.50	A	0.50	A	0.50
2	Varnolene	A	0.50	A	0.50	E	1.25	A	0.50	N	3.40	A	0.50	E	1.25	D	1.00
3	Kerosene	A	0.50	E	1.25	K	2.75	C	0.85	V	8.84	D	1.00	N	3.40	M	3.20
4	Torch Oil	U	6.27	Y	17.6	Sed		Z1	27.0	Sed		X	12.9	V	8.84	X	12.9
5	Solvent Naphtha No. 54	A	0.50	A	0.50	A	0.50	A	0.50	H	2.00	A	0.50	A	0.50	A	0.50
6	Solvent Naphtha No. 55	A	0.50	A	0.50	B	0.65	A	0.50	H	2.00	A	0.50	A	0.50	A	0.50
7	V. M. P. Naphtha	A	0.50	A	0.50	B	0.65	A	0.50	J	2.50	G	1.65	A	0.50	A	0.50
8	Varsol No. 2	A	0.50	A	0.50	D	1.00	B	0.65	P	4.00	A	0.50	D	1.00	C	0.85
9	Solvesso No. 1	A	0.50	A	0.50	A	0.50	A	0.50	F	1.40	A	0.50	A	0.50	A	0.50
10	Solvesso No. 2	A	0.50	A	0.50	A	0.50	A	0.50	J	2.50	A	0.50	A	0.50	B	0.65
11	Solvesso No. 3	A	0.50	A	0.50	H	2.00	E	1.25	T	5.50	C	0.85	G	1.65	G	1.65
12	Solvesso No. 4	C	0.85	B	0.65	O	3.70	H	2.00	X	12.9	J	2.50	R	4.70	M	3.20
13	Petrobenzol	A	0.50	G	1.65	A	0.50	A	0.50	D	1.00	A	0.50	A	0.50	K	2.75
14	Troluoil	A	0.50	A	0.50	A	0.50	A	0.50	F	1.40	A	0.50	A	0.50	A	0.50
15	Apcothinner	A	0.50	A	0.50	A	0.50	A	0.50	H	2.00	A	0.50	A	0.50	A	0.50
16	Apco 125	A	0.50	A	0.50	C	0.85	A	0.50	Q	4.35	A	0.50	E	1.25	D	1.00
17	Apco B-75	A	0.50	A	0.50	E	1.25	A	0.50	P	4.00	A	0.50	F	1.40	G	1.65
18	Sunoco Spirits	A	0.50	A	0.50	E	1.25	A	0.50	R	4.70	A	0.50	D	1.00	D	1.00
19	Special Sunoco Spirits	A	0.50	A	0.50	A	0.50	A	0.50	Q	4.35	A	0.50	D	1.00	D	1.00
20	Sinclair Rubber Solvent	A	0.50	A	0.50	A	0.50	A	0.50	Sed		A	0.50	A	0.50	A	0.50
21	Sinclair Naphthol	A	0.50	A	0.50	C	0.85	A	0.50	Sed		A	0.50	A	0.50	A	0.50
22	Sinclair VMP Naphtha	A	0.50	A	0.50	B	0.65	A	0.50	H	2.00	A	0.50	A	0.50	A	0.50
23	Sinclair Solvent	A	0.50	A	0.50	E	1.25	A	0.50	Q	4.35	A	0.50	C	0.85	D	1.00
24	Sinclair Odorless Insecticide Base	A	0.50	C	0.85	Sed		D	1.00	Sed		D	1.00	P	4.00	M	3.20

Viscosity values refer to the Gardner-Holdt Bubble Viscosity tubes. Poises refer

ous return of copal oil to the melt has an effect upon the final condition of the resin. Refluxing is an aid to running, but at the expense of the product's hardness. In the series under study, the amount of refluxing was such that the resins run with the greatest losses in weight had softening points not much above room temperature. It appears, however, that the resins when used as films gain hardness in a short time. This was apparently confirmed by performing hardness determinations on films of each of the run resins. The Sward hardness rocker was used on films which had been deposited from toluol solutions. No oil was present. Film hardnesses as determined after 1, 3, and 7 days are given in Table LI.

IN VARIOUS PETROLEUM SOLVENTS

No. 21 Selected Nubs Ordinary		Pale East India Macassar Nubs		Pale East India Singapore Nubs		Kauri No. 2 Pale		Kauri No. 2 Brown		Manila Loba C		Manila CBB		Manila DBB		Philippine Manila Bold Pale Chips		Pontianak Bold Scraped	
Viscosity	Poise	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise	Viscosity	Poise
A	0.50	A	0.50	Sed		A	0.50	C	0.85	B	0.65	A	0.50	A	0.50	A	0.50	A	0.50
D	1.00	A	0.50	Sed		C	0.85	F	1.40	G	1.65	E	1.25	A	0.50	C	0.85	H	2.00
K	2.75	G	1.65	Sed		H	2.00	G	1.65	R	4.70	A	0.50	R	4.70	K	2.75	J	2.50
W	10.70	Z	22.7	Sed		V	8.84	W	10.70	Sed		Z	22.7	W	10.70	Z1	27.0	S	5.00
A	0.50	A	0.50	Sed		A	0.50	B	0.65	A	0.50	A	0.50	A	0.50	A	0.50	A	0.50
A	0.50	A	0.50	Sed		A	0.50	G	1.65	A	0.50	A	0.50	A	0.50	A	0.50	B	0.65
A	0.50	A	0.50	A	0.50	A	0.50	K	2.75	B	0.65	A	0.50	A	0.50	A	0.50	B	0.65
C	0.85	A	0.50	D	1.00	C	0.85	S	5.00	E	1.25	E	1.25	D	1.00	C	0.85	H	2.00
A	0.50	A	0.50	A	0.50	A	0.50	C	0.85	A	0.50	A	0.50	A	0.50	A	0.50	A	0.50
B	0.65	B	0.65	B	0.65	C	0.85	D	1.00	C	0.85	C	0.85	A	0.50	A	0.50	C	0.85
H	2.00	E	1.25	H	2.00	B	0.65	J	2.50	K	2.75	G	1.65	J	2.50	K	2.75	S	5.00
R	4.70	O	3.70	T	5.50	N	3.40	Q	4.35	S	5.00	U	6.27	P	4.00	O	3.70	U	6.27
E	1.25	A	0.50	Sed		A	0.50	C	0.85	A	0.50	A	0.50	A	0.50	A	0.50	A	0.50
A	0.50	A	0.50	Sed		A	0.50	D	1.00	A	0.50	B	0.65	A	0.50	A	0.50	B	0.65
A	0.50	A	0.50	Sed		A	0.50	B	0.65	B	0.65	A	0.50	A	0.50	A	0.50	A	0.50
E	1.25	C	0.85	Sed		D	1.00	G	1.65	K	2.75	G	1.65	G	1.65	F	1.40	G	1.65
G	1.65	C	0.85	Sed		C	0.85	G	1.65	G	1.65	H	2.00	F	1.40	H	2.00	P	4.00
F	1.40	C	0.85	F	1.40	C	0.85	G	1.65	E	1.25	F	1.40	F	1.40	D	1.00	G	1.65
E	1.25	C	0.85	Sed		C	0.85	E	1.25	G	1.65	G	1.65	D	1.00	F	1.40	F	1.40
A	0.50	A	0.50	D	1.00	A	0.50	E	1.25	A	0.50	A	0.50	A	0.50	A	0.50	A	0.50
A	0.50	A	0.50	F	1.40	A	0.50	C	0.85	A	0.50	A	0.50	A	0.50	A	0.50	A	0.50
A	0.50	A	0.50	Sed		A	0.50	G	1.65	A	0.50	A	0.50	A	0.50	A	0.50	C	0.85
D	1.00	A	0.50	C	0.85	C	0.85	R	4.70	D	1.00	E	1.25	E	1.25	G	1.65	K	2.75
P	4.00	H	2.00	Sed		H	2.00	E	1.25	R	4.70	N	3.40	O	3.70	M	3.20	U	6.27

to approximate absolute viscosities. Sed a sediment formed in the solution on standing.

Commercial Thermal Processing Procedures. An ideal running procedure would see the resin held at the proper temperature for as short a period as possible to avoid darkening in color and undesirable secondary reactions. Modern practice seeks to obtain this by the use of agitation, inert atmospheres, instruments for accurate temperature regulation, cooling devices, and the proper metals of construction.

With the accretion of data on the chemistry of running combined with the advancing knowledge of heat transfer, the running operation has passed from the use of the old type pot to closed vessels of the autoclave type.

The old type, heavily constructed pots are not suitable for the

TABLE XLVII

PHYSICAL AND CHEMICAL PROPERTIES OF RUN RESINS

Name of Resin	Per Cent Loss	Softening Point		Melting Point		Specific Gravity	Direct Acid Number	Indirect Acid Number	Saponification Number	Iodine Number
		°C.	°F.	°C.	°F.					
Batavia damar, A/D	10	80	176	120	248	1.04	13	17	22	107
Batavia damar, A/E standard	10	70	158	110	230	1.04	10–15	17	15	119
Batu east india nubs and chips	10–15	95–115	203–239	135–160	275–320	1.04	15	33	36	95
Black east india bold scraped	10–15	110–120	230–248	135–145	275–293	1.03	12–15	14	36	88
Boea hard bold amber	20–25	105	221	125–135	257–275	1.06	78–85	86	91	106
Congo No. 1 water-white transparent	25	70–80	158–176	110–120	230–248	1.04	40–60	53	64	88
Congo No. 4 pale bold straw	25	80–90	176–194	105–110	221–230	1.05	60–80	75	82	89
Congo No. 11 hard dark amber bold	25	80–90	176–194	115–125	239–257	1.04	60–75	68	72	85
Congo No. 21 selected nubs ordinary	25	80–90	176–194	115–125	239–257	1.05	60–75	76	81	85
Kauri No. 2 brown	20–25	80–90	176–194	120–130	248–266	1.06	12–20	16	27	79
Kauri No. 2 pale	20–25	80	176	120–130	248–266	1.06	20–30	21	36	87
Manila CBB	25	80–90	176–194	115–120	239–248	1.06	60	67	70	99
Manila DBB	25	85–90	185–194	125–135	257–275	1.05	50–60	53	67	96
Manila loba C	20	85–90	185–194	125–130	257–266	1.05	55–65	72	89	104
Pale east india Macassar nubs	10–15	100	212	140–145	284–293	1.04	12–15	22	21	95
Pale east india Singapore nubs	10–15	110	230	135–140	275–284	1.04	9–14	16	17	89
Philippine manila bold pale chips	20	85	185	127	261	1.06	50–55	62	72	93
Pontianak bold scraped	20–25	105	221	125–130	257–266	1.06	75–85	92	86	99

These figures are merely typical.

TABLE XLVIII

Changes in Physical and Chemical Constants of Natural Resins on Running

Resins	Softening Point °C.	Softening Point °F.	Melting Point °C.	Melting Point	Direct Acid Number	Indirect Acid Number	Saponification Number	Iodine Number
Pale east india Macassar nubs	−10	−18	6	11	−11	− 9	− 26	15
Pale east india Singapore nubs	− 7	−13	− 6	− 11	−16	− 19	− 16	10
Batu east india nubs and chips	−32	−57	2	4	−15	− 8	− 15	24
Black east india bold scraped	− 4	− 7	−24	− 43	− 8	− 20	− 1	5
Batavia damar A/E	0	0	7	13	−15	− 14	− 14	7
Batavia damar A/D	5	9	−13	− 23	−14	− 17	− 12	− 2
Macassar manila loba C	9	16	7	13	−72	− 80	− 76	−21
Macassar manila CBB	8	14	−10	− 18	−73	− 97	−106	−21
Macassar manila DBB	7	13	9	16	−90	−110	−112	−16
Manila bold pale chips (Philippine)	− 6	−11	− 2	− 4	−60	− 81	− 82	−27
Pontianak bold scraped	18	32	− 7	− 13	−39	− 39	− 63	−26
Boea hard bold amber	25	45	6	110	−45	− 61	− 68	−23
Kauri No. 2 pale	−25	−45	− 6	− 11	−48	− 67	− 58	−33
Kauri brown No. 2	−40	−72	−12	− 21	−56	− 65	− 57	−35
Congo No. 1 water-white transparent	−17	−30	−20	− 36	−59	− 62	− 60	−27
Congo No. 4 pale bold straw	2	4	−67	−120	−37	− 43	− 44	−44
Congo No. 11 hard dark amber bold	−11	−20	−94	−133	−39	− 52	− 51	−38
Congo No. 21 selected nubs ordinary	− 6	−11	−43	− 78	−37	− 48	− 46	−39

Changes are positive unless otherwise marked.

TABLE XLIX

Decrease in Acidity of East India Resins on Running to Different Weight Losses

Resin	Direct Acid No. Original	Direct Acid No. 12½% Loss	Direct Acid No. 18% Loss	Indirect Acid No. Original	Indirect Acid No. 12½% Loss	Indirect Acid No. 18% Loss
Pale east india Macassar bold	19	16	14	27	22	17
Pale east india Macassar nubs	22	18	14	32	25	19
Pale east india Singapore bold	20	14	11	37	21	15
Black east india bold scraped	20	17	16	36	24	21

TABLE L

PROPERTIES OF CONGO RESIN RUN TO DIFFERENT LOSSES

Experiment Number	Minutes until First Drop of Distillate Came Over	Minutes for Collection of Distillate	Maximum Temperature of Melt	Maximum Temperature of Vapors	Per Cent Total Loss of Resin	Per Cent Resin Obtained as Distillate	Per Cent Resin Lost as Vapor	Run Resin: Softening point	Run Resin: Melting point	Run Resin: Acid number: Direct	Run Resin: Acid number: Indirect
1	20	30	..	245°C.	15	11	4	80°C.	120°C.	75	83.6
2	45	105	355°C.	230°C.	15	10.6	3.4	72°C.	105°C.	66.2	76.8
3	25	100	355°C.	235°C.	15	10.3	4.7	72°C.	105°C.	62.0	68.0
4	35	120	360°C.	240°C.	19.5	15	4.5	66°C.	98°C.	53.1	60.6
5	30	175	360°C.	235°C.	23.3	17.5	5.8	62°C.	94°C.	50.8	55.5
6	35	135	374°C.	240°C.	26.5	20	6.5	64°C.	100°C.	54.8	60.6
7	30	160	376°C.	242°C.	28 8	22.5	6.3	58°C.	96°C.	51.8	59.5
8	25	145	386°C.	255°C.	31 3	25	6.3	70°C.	104°C.	53.1	62.2
9	25	150	390°C.	270°C.	35 8	30	5.8	50°C.	88°C.	43.7	52.7
10	30	155	396°C.	265°C.	41.5	35	6.5	40°C.	82°C.	37.5	46.0
Original, unrun congo No. 11								105°C.	205°C.	86.2	110.5

TABLE LI

FILM-HARDNESS DETERMINATIONS ON CONGO RUN TO DIFFERENT LOSSES

Lot Number	Per Cent Running Loss	Sward Hardness Ratings*: After 1 day	After 3 days	After 7 days
1	15	32	50	58
2	15	26	60	60
3	15	26	52	60
4	19.5	28	62	70
5	23.3	30	64	72
6	26.5	26	60	74
7	28.8	26	52	68
8	31.3	30	50	68
9	35.8	28	64	82
10	41.5	40	64	88

* 100 equals the hardness of plate glass.

methods of running dictated by present-day knowledge of the chemical changes involved. These pots were designed principally to withstand the terrific heating then used in the processing of fossil resins. The process actually came closer to being one of "roasting" rather than one of melting. The pots possessed two chief drawbacks: Their heavy construction was a definite disadvantage when a rapid lowering of temperature was necessary, and the shape, usually of a tall, narrow nature (see Fig. 39), resulted in uneven heat transmission throughout the charge, the resin near the heating surface being over-run and the remainder sometimes being under-run. The danger of this was recognized by varnish makers and somewhat mitigated by the practice of "greasing" or "buttering" the kettle with rosin. In this manner, the easily melted rosin formed a liquid layer on the bottom of the kettle in which the resin dissolved. Because the presence of rosin could not be tolerated in all varnishes, it was necessary to combat uneven heating in another way. This was done by the use of vessels of a squatter form to give more heating surface for the same amount of useful volume. A modern running kettle is shown in Fig. 40.

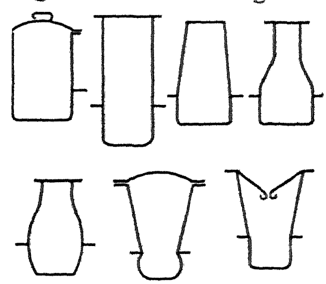


FIG. 39. Old-fashioned resin running pots. (After Livache.)

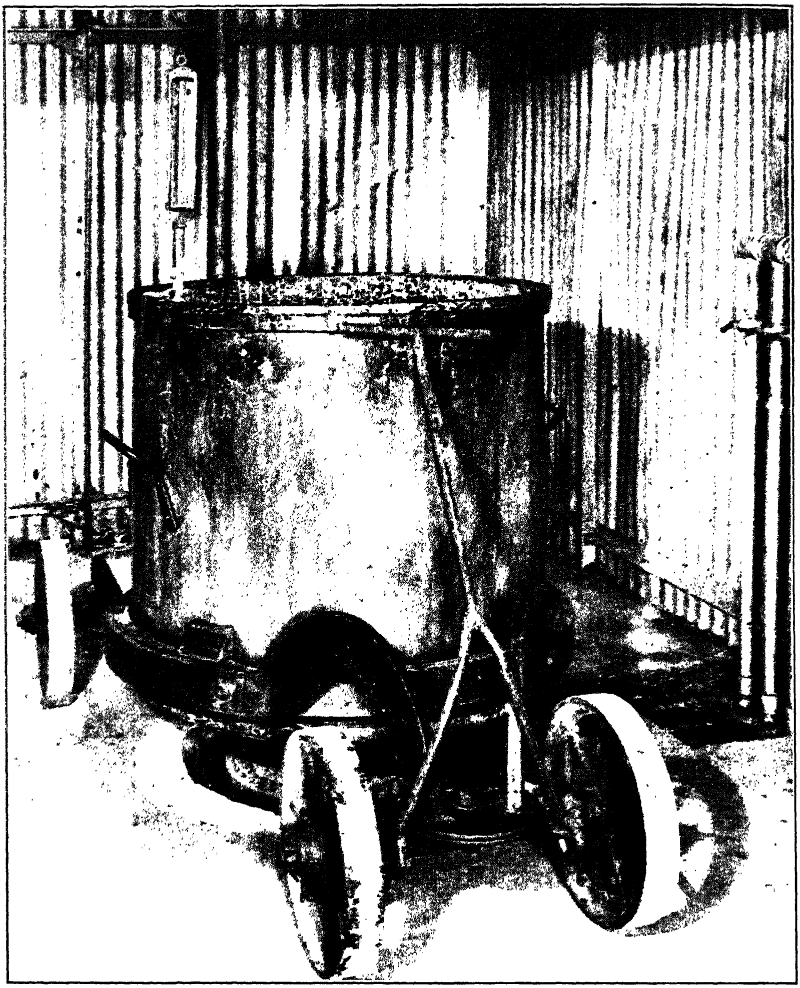
The amount of resin that can be processed in an ordinary varnish kettle is limited by the foam capacity of the vessel. The fact that running is attended by the generation of a large amount of foam makes it imperative that the original resin charge occupy less than 25 per cent of the total volume. It is not unusual for the volume of foam to treble that of the resin.

On a small scale, 100-lb. batches can be readily handled. With competent operators, they may be carried to 200 or 300 lb., but amounts greater than this demand special apparatus.

On a large scale, commercial operation in the United States, but more particularly abroad, employs equipment capable of processing 1 to 5 tons. Closed kettles are the preferred equipment. These employ inert atmospheres such as CO_2 (to give paler products), mechanical or gas agitation, careful temperature control, and uniform heating.

The inert gas generator produces an inert gas by the combustion within closed chambers of controlled mixtures of gas and air. The products of combustion, when purified and scrubbed, can be used for the prevention of darkening during the running of resins or the cooking

of varnishes, the elimination of skinning of paint and varnish during storage, and the prevention or extinguishing of fires. Figure 41 shows a



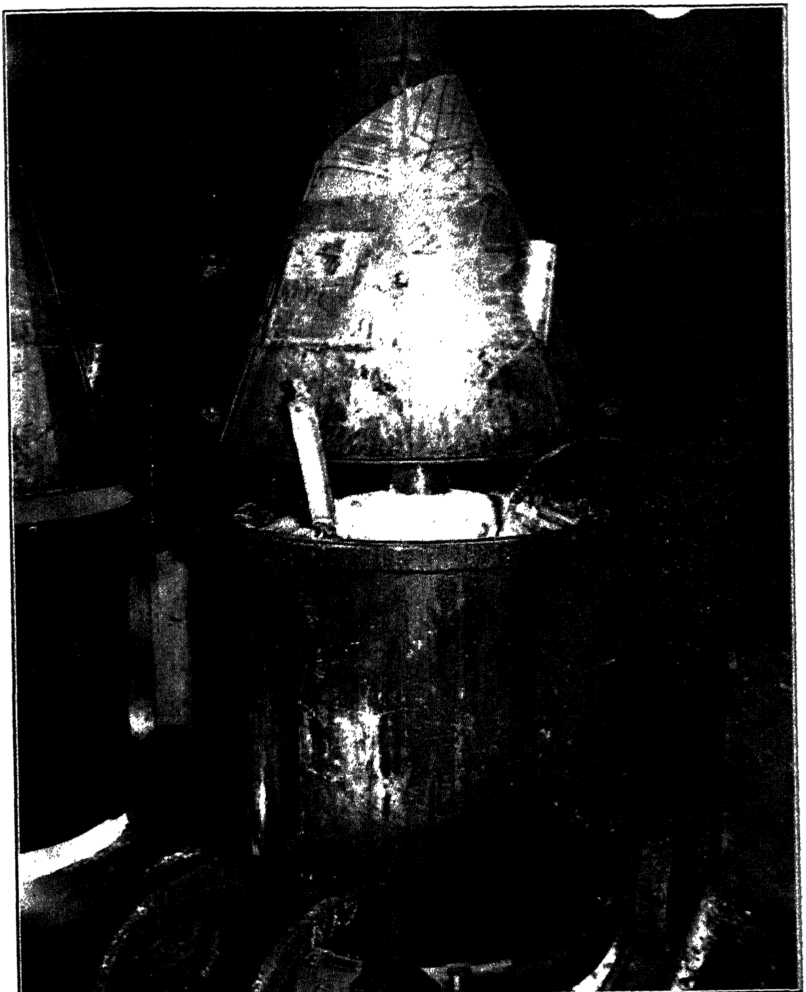
Courtesy International Nickel Co., Inc.

FIG. 40. Portable copper kettle with brazed Monel bottom. A gas heating unit is shown.

varnish kettle equipped with hood and cover for application of an inert gas.

Appearance during Running. When a resin is run it undergoes definite physical changes under the influence of the applied heat. The

time period necessary to melt the resin obviously depends upon its hardness and usually takes about one hour. Once the resin has been



Courtesy Industrial Gas Section, American Gas Association

FIG. 41. Varnish cooker using a blanket of inert gas. The cover merely rests on top of the kettle but may be clamped down if necessary. The gas induction pipe can be seen at the right. During most operations, gas is bubbled through the batch continuously.

converted to a liquid state, further heating is necessary to decompose the dicarboxylic acids into monobasic acids which are oil soluble.

During this latter period the viscosity of the liquid resin decreases from a quite heavy liquid to a thin fluid resembling hot oil.

To be oil soluble the liquid should run off the paddle as smooth, free drops in the manner of thin, hot oil and should be entirely free from any ropy, lumpy, or stringy appearance. Both liquid and paddle must be hot to give a clean drip.

The running of a resin is accompanied by the evolution of gas and the distillation of copal oil. Water vapor is also given off. This is due chiefly to the moisture present in the resin, although some is formed as a result of anhydride formation. Experiments performed on the same resin carried to different weight losses show that the variation in the amount of water distilled is small. Likewise, the amount of non-condensable gases formed is fairly constant over a wide range of running losses.

The evolution of gas, moisture, and copal oil is attended by a considerable degree of foaming and provision must be made to control it. "Heading" is excessive foaming which tends to rise out of the kettle. On a normal kettle-size batch it is controlled by the use of vessels of sufficient capacity and by beating down ("whipping") the foam with a paddle or flexible metal rod. On a large scale, completely enclosed vessels are employed. Foam is controlled by mechanical agitation, superheated steam, and pressure.

Foam is not a measure of the total amount of vapors evolved. The amount of foam present at any time depends upon the relative rates of evolution and breaking of foam. If the resin is heated slowly at low temperatures, the foam breaks almost as soon as it forms. When heated at higher temperatures, a shorter running time is needed, but the foaming is excessive because bubbles are formed more quickly than they break.

Some operators prefer to bring the resin up to the maximum temperature in several steps, with intermediate cooling or "breathing" periods. The foam is allowed time to subside. The cooling of the kettle walls also permits a larger amount of copal oil to be returned to the melt.

Resins pass through a definite series of physical changes which are similar for all cases in which run resins are produced. For example, the observations in Table LII were made for an open-kettle run of congo.

For resins other than congo, similar changes occur, but at different times and at different temperatures. In closed kettles, the appearance of the resin during the run is similar to that witnessed in open-kettle runs.

The influence of temperature, so far as the general appearance of the

TABLE LII

Description of an Open-Kettle Congo Run at 344°C. Which Was Held until Oil Soluble

Time in Minutes	Temperature		Appearance of Resin
	°C.	°F.	
5 to 10	100–150	212–302	Very small amount of smoke evolved.
15	200	392	Resin softening a little in bottom of kettle.
20	225	437	Much smoke. Part of resin becoming spongy.
25	250	482	Able to stir resin for first time. Both spongy and hard lumps.
30	270	518	Spongy lumps. Able to stir more easily; much smoke; beginning to foam.
35	290	554	Spongy lumps. Foam now doubles original volume of resin.
40 to 45	305–320	581–608	Spongy lumps. Foam increasing slowly.
50 to 60	330–340	626–644	Spongy lumps decreasing. Foam now triples original volume.
65	344	651	Very few spongy lumps remain. Foam down to double volume.
70	344	651	Spongy lumps all gone. Liquid now only equals original resin volume. Liquid is like much over-bodied China wood oil.
75	344	651	Foam nearly all gone. Liquid about like a 50:50 mix of over-bodied China wood oil and medium-bodied linseed. Loss in wt. 21½ per cent.
90	344	651	Liquid does not quite give a clean drip from paddle —is about like medium-bodied linseed oil. Loss in wt. 30 per cent.
100	344	651	Clean drip from paddle. Liquid is like thin-bodied linseed oil. Resin is now completely soluble in oil. Loss in wt. 35 per cent.

resin during running is concerned, is primarily in the speed of the change and on the quantity of foam present at any one time. This can be seen from Table LIII.

Agitation. During the running of resins, a film forms on the inside of the vessel, which film retards the transfer of heat. Unless the sides and bottom of the vessel are scraped regularly during the heating process, a film of low thermal conductivity remains between the heating source and the material to be heated. The effect is loss of heat and local overheating within the film, resulting in darkening and undesirable sec-

TABLE LIII

OPEN-KETTLE CONGO RUNS

NUMBER OF MINUTES TO REACH VARIOUS STAGES IN RUNNING

Max. Temp. Reached °F.	Min. to Reach Max. Temp.	Min. till Spongy Lumps All Gone	Min. at Max. Temp. Req. till Oil Soluble	Total Min. for Runs	Max. Amount of Foam Observed	Per Cent Loss in Weight
400	30	..	..	300*	None	1.7
500	40	..	..	480†	A little	25.0
550	50	125–180	250	300	Double volume‡	30.0
575	50	50–75	160	210	"	32.5
600	60	75	105	165	Triple volume	33.3
625	65	70–80	65	130		33.3
650	65	70	35	100		35
675	70	70	..	90		35
700	65	65	..	65		35

* Stopped because temperature was too low to run the congo.

† Oil solubility was not reached in 8 hours.

‡ The total volume in the kettle was twice the original volume of the resin.

The last three runs were not quite the same as the earlier ones as they were from another group which was held at maximum temperature till 35 per cent loss in weight was reached.

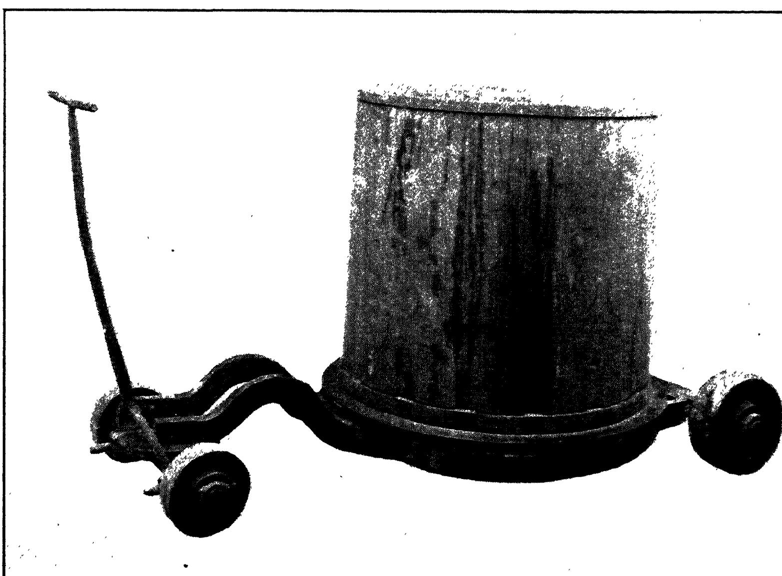
ondary reactions. Modern running vessels are equipped with stirring or scraping devices to eliminate or moderate film formation. The speed of agitation varies with the progress of the run and is set by the operator according to his experience.

Resin Size. The size of the resin pieces fed to the processing kettle is important if local overheating is to be avoided. On a small scale, better results are obtained by using ground resin. The time of running is reduced. On the average varnish scale, it is not necessary to reduce the resin beyond a 2-inch size. For large batches, cracking the large lumps of resin is an advantage. Reducing beyond this size does not shorten the heating period to any worth-while extent.

Danger of Fumes. Danger from the breathing of fumes formed during the running of natural resins is not mentioned in the references on industrial hazards. As the fumes are inflammable, insurance companies generally demand that they be exhausted from the room or building. In the most modern plants engaged in copal running, processing is done in closed vessels and the fumes evolved are passed through scrubbers.

Courtesy International Nickel Co., Inc.

FIG. 42. Varnish stacks with kettles in place.



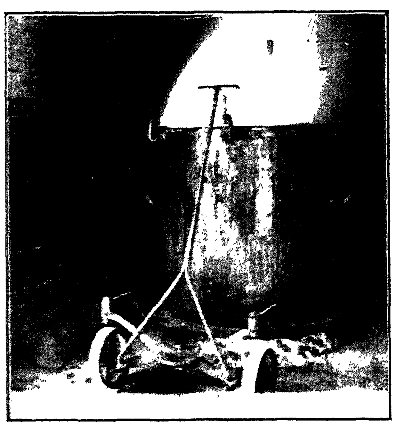
Courtesy International Nickel Co., Inc.

FIG. 43. Modern 200-gallon kettle made of nickel-clad steel (40 in. by 42 in.).

When resins are run in ordinary varnish kettles the heating is done in a "varnish stack." The varnish stack consists of one or more hoods connected by small flues to a common central stack (see Fig. 42). The hood may be a simple metal canopy or it may be a small three-sided room large enough to accommodate the kettle. The kettles are mounted on carriages (see Fig. 43) to permit easy moving to and from the hood. Heating is provided through a grate centrally located in the floor of the hood. The fumes were formerly allowed to escape to the atmosphere, with the accumulation of explosive gaseous mixtures prevented by the maintenance of a small flame in each of the flues to burn the gases gently as formed. Often the fumes are passed through water sprays which condense the copal oil. After the copal oil-water mixture is allowed to settle, the supernatant layer of oil is drawn off. The water remaining is returned for reuse.

The effect of materials of construction on color is discussed in Chapter XII on the physical and chemical properties of the natural resins.

Method of Heating. Running operations are usually performed with oil as the fuel. The burners are easily and quickly regulated, with

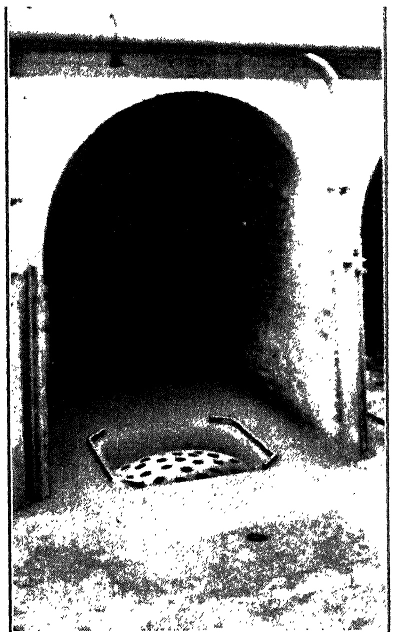


Courtesy Hilo Varnish Corporation

FIG. 44. Old style heating over an open coke fire.

elimination of the time lag that characterized the coke and charcoal firing methods (see Fig. 44) formerly in vogue. The use of manufactured gas and electric heating is generally avoided because of the greater cost, but natural gas is sometimes used in localities where this resource abounds. In a number of plants reclaimed copal oil is burned along with the regular fuel oil.

A modern mechanism for cooking varnishes or running resins is the radiant heater employing a ceramic dome (Fig. 45). Fuel is ignited, mixed with air, and expanded by the heat to a high pressure in the tunnel of the unit. A premixture of fuel and air (already in the first stages of combustion) is brought to the heating chamber. Upon leaving



Courtesy International Nickel Co., Inc.

FIG. 45. Ceramic dome of a radiant type heater.

the tunnel, the mixture is expanded into a larger heating chamber where combustion is completed to produce incandescence. The ceramic dome covering the heating chamber likewise becomes incandescent and radiates heat uniformly over the kettle bottom. No flame is visible and the combustion is characterized by a rapid succession of miniature explosions.

Although most of the natural resins are still processed in kettles, large manufacturers resort to the use of completely enclosed units similar to those used in synthetic resin manufacture. Such units are in use handling an average batch of 1 to 2 tons. As well-controlled running is the first step in the preparation of copal esters, copals prepared for

such use are processed in these units. Esterification is carried out in the same vessel by adding glycerin to the melted mass.

A sketch is given in Fig. 46. Sommer[21] claims rapid and uniform running of the resin with the elimination of dangerous foaming and fire hazards, by the use of stirring devices and rapid exhaustion of vapors.

In the Walpamur[22] process, superheated steam is passed into the molten mass through numerous openings in the stirring arms. It is claimed that the use of superheated steam is effective in breaking down the froth. It is important that the temperature of the steam be not less than that of the melted resin.

Refluxing. Unduly emphasized criticism has been directed to the running of natural resins before use in oil varnishes. The weight losses are represented as a financial drawback not encountered in the preparation of synthetic resin varnishes. Even well-known "100-per cent phenolic resins" cede 6 to 35 per cent of their original weight upon incorporation with oils.[23]

Natural resins can be made oil soluble with greatly reduced losses by simple refluxing of the resin. Experiments have been performed in which congo and loba were rendered oil soluble by refluxing at temperatures ranging from 625°F. for 1 hour, down to 260°F. for 10 hours. The losses were from 5 to 10 per cent by weight.

The resin was ground to a small size and heated in a kettle fitted with a reflux condenser. The temperature was raised as quickly as possible to 625°F. and held there until the resin became oil soluble. All condensable vapors were returned to the kettle. Non-condensable gases come off during the early period of heating. For best results, agitation should be provided.

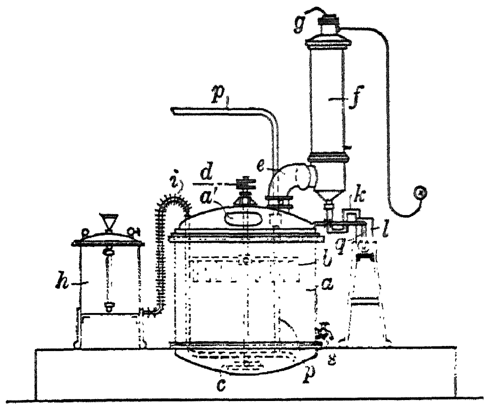
The refluxed resin was made into a 15-gallon linseed oil varnish and compared for drying properties with a normal varnish containing the same amount of driers and thinners. Both dried and hardened similarly.

In other work, a sealed condenser with a blow-off valve for pressure relief was employed. The thermal processing was done under 2 to 3 atmospheres (15 to 30 pounds per square inch gage). Kettle construction must be sturdy enough to withstand such pressures. The pressure-relief valve was set at 30 pounds per square inch and allowed the release of non-condensable gases.

[21] J. Sommer, U. S. Patent 1,960,855 (1934).

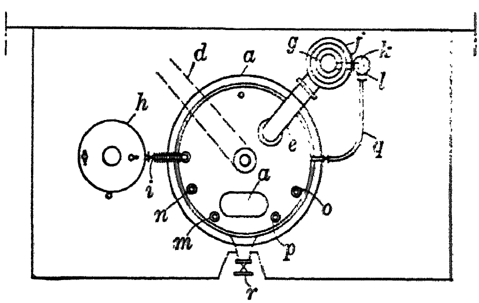
[22] British Patent 457,076 (1936).

[23] These figures were obtained by heating 10 grams of resin at 560°F. for 15 minutes.



Elevation

Plan view of stirrer



Plan view

Fig. 46. Sommer melting and esterifying apparatus.

a Boiler
a′ Manhole opening
b Foam divider
c Centrifugal stirrer
d Drive
e Vapor
f Tubular cooler
g Condensate collector
h Glycerin reservoir
i Glycerin feed tube
k Connecting tube between condenser and separator
l Glycerin separating vessel
m Air admission valve
n Thermometer
o Thermometer
p Movable gas feed tube
q Return of glycerin to boiler
r Discharge cock
s Sampling cock

E. Mertens[24] ran congo under a reflux condenser and obtained a light-colored, oil-soluble, uniform product with a loss of 8 per cent. The copal was maintained in thin layers below 315°C. Solution of congo in oils was effected without loss at 290 to 300°C. in an autoclave under 88 to 110 lb. per sq. in. pressure, using a nitrogen atmosphere. The solution had poor drying properties.

Numerous investigators have attempted modification or simplification of the running procedure. In general, the attempts have not met with success. Invariably a roundabout process was devised which did not eliminate running, but merely achieved it indirectly and with greater complexity.

Processes have been studied in which direct solution in solvents was accomplished by heating under pressure. Schützenberger[25] and Strange, Graham and Burrel[26] were granted patents covering such methods. Oil was heated along with the resin and solvent to form the varnish in one operation. The products were of an unsatisfactory color and uniform results could not be secured.

A favorite line of investigation was the heating of resin under pressure in a medium whose boiling point at the pressures used was above the temperature of operation. The use of naphthalene for this purpose is discussed by Coffignier.[27] Several patents were issued for this process[28] and the method was in industrial use from 1906 to 1910.

Pyhälä[29] heated powdered Zanzibar copal with 20 to 30 per cent of its weight of a mineral oil whose boiling point was above the melting point of the resin. After the evaporation of mineral oil, a pale resin was obtained. The product was soluble in turpentine and previously bodied linseed oil. Pyhälä's results, however, have been adversely criticized by Scheifele[30] on the grounds that complete running of the copal and complete removal of mineral oil were not shown.

Stiel[31] claims that finely powdered congo can be rendered alcohol soluble by exposure to an oxidizing atmosphere. The pulverized resin is placed in a rotating drum through which is passed a stream of moist

[24] *Bull. inst. R. colon. belge*, 4, 268-91 (1933); *Chimie & industrie*, 31, 635.

[25] French Patent 16,472 (1856).

[26] French Patents 320,630 (1902) and 441,581 (1910).

[27] C. Coffignier, "Varnishes, Their Chemistry and Manufacture," Scott, Greenwood & Son, London, 1923.

[28] Crebert, French Patent 334,107 (1903); H. Terisse, French Patent 334,300 (1904); H. Terisse and C. Coffignier, French Patent 395,785 (1909).

[29] E. Pyhälä, *Farben-Ztg.*, 34, 1552-3 (1929).

[30] B. Scheifele, *Farben-Ztg.*, 34, 1786 (1929).

[31] A. Stiel, German Patent 548,394 (1929).

air at elevated temperatures for several days. Under this treatment the copal is gradually oxidized to an alcohol-soluble form. The process was a failure in actual production because the products yielded solutions of a deep reddish color.

Mastication of Copals. Krumbhaar has been granted patents[32] on a process for rendering fossil copals soluble by masticating between rollers. The product of this treatment is converted to a form soluble in organic solvents, but not to an oil-soluble condition. Running is more easily performed on a masticated copal than on an untreated one. The solubility of finely powdered hard copal can be increased by masticating between hot steam-heated rolls. This may be due to a partial breakdown, by mechanical forces, of the molecular structure of the resin. In the operation, copal becomes soft and plastic at about 200°F. The mass is then rolled out to thin films which are returned to the rolls for repeated treatment. The action is so severe, especially at temperatures of 250 to 300°F. and under the pressure of closely spaced rolls, that the copal becomes soluble in propyl, butyl, and amyl alcohols. The viscosity of the resulting solutions decreases with longer periods of mastication.

It might appear that more effective weakening of the resin's internal structure could be secured by running the rolls at different speeds to take advantage of the shearing action. Friction between rollers, however, becomes so great that the greatest pressure is applied only by rolls set at equal speeds. The process finds application as the first step in the preparation of run or esterified congos.

Mastication also increases the reactivity of resins, i.e., inter-reaction with metallic oxides can be effected at comparatively low temperatures with pale products resulting. Whereas low-temperature mastication improves the solubility, high-temperature mastication promotes reactivity. The mastication may be performed with mixtures of resins, in combination with oils, in the presence of solvents (under a reflux condenser), or in ball mills rather than on roller mills.

Copal Oil. The oily portion of the liquid distillate obtained from the running of natural resins has been given the name "copal oil." The distillate from non-copals also goes under this name. When the liquid products of running are condensed and retained, two immiscible liquid layers are obtained. The supernatant oily layer is the copal oil portion and is the valuable component of the distillate. The water layer, usually containing traces of acids and aldehydes, is discarded.

Studies of copal oil have been the starting points for the determina-

[32] W. Krumbhaar, U. S. Patent 2,007,333 (1935); British Patent 457,637 (1936).

tion of the reactions involved in running. Numerous investigations have produced considerable data on its composition. Terpenic bodies appear to be the chief compounds present. Pinene, β-pinene, limonene, dipentene, and camphene have been reported many times.

Schmölling[33] reported the constants shown in Table LIV for two samples of kauri and Manila copal oils:

TABLE LIV

	Kauri Copal Oil	Manila Copal Oil
Specific gravity (15°C.)	0.8677	0.9069
Acid value	3.0	28.3
Saponification value	4.9	45.7
Ester value	1.9	17.4
Iodine value	288.9	230.4

Gill and Nishida[34] found kauri copal oil to be almost insoluble in water, but very soluble in ethyl alcohol, glacial acetic acid, ether, chloroform, carbon disulfide, carbon tetrachloride, benzene, and mineral spirits. When spread out on a glass plate in thin layers and exposed to the air, it gradually solidified to a resinous film within five to six days. The original oil possessed the following constants:

Specific gravity (20°C.)	0.9667
Flash point (Pensky-Marten)	85 – 86°C.
Specific rotation $[\alpha]^{20}_{D}$	+3°, 40′
Specific viscosity (Engler, 20°C.)	11.8
Refractive index (25°C.)	1.5128
Acid value	69.0
Saponification value	83.0
Iodine value (Hanus, 15 minutes)	114.0

Upon neutralization with 10 per cent potassium hydroxide and subsequent washing and dehydration, a straw-yellow transparent oil was obtained with a yield of 52 per cent. The refined oil had the drying properties of the original and the following characteristics:

Specific gravity (20°C.)	0.9280
Specific rotation $[\alpha]^{20}_{D}$	+2°, 46′
Specific viscosity (Engler, 20°C.)	1.7
Refractive index (25°C.)	1.5102
Iodine value (Hanus, 15 minutes)	104.0

[33] L. Schmölling, *Chem.-Ztg.*, **29**, 955 (1905).
[34] A. H. Gill and D. Nishida, *Ind. Eng. Chem.*, **15**, 1276 (1923).

Pinene and limonene were found together with evidence suggesting the presence of sesquiterpenes and polyterpenes.

The authors have subjected a number of the East India resins to high-vacuum distillation at temperatures below 310°C. (590°F.). Heating was continued until the distillation of liquid ceased. Under the prevailing conditions of temperature and pressure, this took from 6 to 7 hours. The distillate was collected, separated from the water present, and fractionated, under atmospheric conditions, into quarters.

Direct acid numbers were run on the original resin, the resin residue, the vacuum distillate, and each of the quarters from the fractionation. These figures, together with data for the runs, are given in Table LV.

TABLE LV

VACUUM DISTILLATION OF EAST INDIA RESINS

	Pale East India Singapore Bold	Pale East India Macassar Bold	Batu Scraped
Per cent resin residue	82.3	80.6	84.6
Per cent distillate collected	11.0	11.7	12.3
Per cent loss	7.7	7.7	3.5
Maximum vapor temperature (°C.)	145	165	160
Maximum resin temperature (°C.)	305	298	290
Minimum vacuum (cm. Hg)	75.4	73.7	73.7
Direct acid numbers			
Original resin	25	27	30
Resin residue	6	20	16
Vacuum distillate	16	17	22
First quarter	33	16	15
Second quarter	6	7	5
Third quarter	7	3	3
Fourth quarter	11	13	6

The resins were completely run, but were dark in color. Reduction in the total acidity of the resins' constituents is evidenced by a comparison of the acid numbers of the original resins with those of the products.

In each the first quarter fraction obtained from the fractionation of the vacuum distillate contained the most acidic portions. The second and third quarters possessed low acid values, whereas the fourth was of a magnitude intermediate to these and the first.

The colors of individual fractions are given in Table LVI.

TABLE LVI

	Pale East India Singapore	Pale East India Macassar	Batu
First quarter	Amber, clear	Brown, clear	Red-brown, clear
Second quarter	Light green, clear	Yellow-green, clear	Dark brown, clear
Third quarter	Dark green, opaque	Green, clear	Green, clear
Fourth quarter	Dark brown, opaque	Dark green, opaque	Dark green, opaque

During the fractionation, yield and temperature were noted for every 2 cc. of distillate. The boiling point curves plotted by means of this data were quite similar; each showed a rapid temperature rise during the distillation of the first 10 per cent, a leveling out in the neighborhood of 260 to 270°C., and a temperature peak close to 300 to 310°C. Figure 47 represents the boiling point curve for the liquid obtained from the vacuum distillation of pale east india Macassar bold.

Various uses have been found for copal oil. Originally regarded as a nuisance by varnish manufacturers, the fumes from resin running are now reclaimed and, if necessary, purified for particular uses. In Germany[35] they are purified in refineries to yield an oil without objectionable odor and of reported acid and saponification values of 60 to 70 and 80 to 90, respectively.

Within the varnish plant itself, copal oil finds a number of applications. It is sometimes used as a fuel under the running or varnish pots. Because of its dipentene[36] content attempts have been made to use it as an anti-skinning agent. Dantlo[37] states that the addition of a little oil to fresh copal facilitates fusion with less loss and a clearer melt. Use as a solvent for varnish, lacquer, shoe polish, rubber, and wood-preserving substances has been reported.[38] Its high calorific value and freedom from sulfur make it suitable as a fuel for certain types of engines. However, its high degree of carbon formation upon being burned is a drawback. It has also been used in the manufacture of putty and core compounds.

The amount of liquid obtained from the running of natural resins

[35] "Copal Oil," *Paint Manuf.*, 368 (1937).

[36] Dipentene is the optically inactive mixture of *d*- and *l*-limonene.

[37] G. Dantlo, *Peintures, pigments, vernis,* 10, 6-7 (1933).

[38] P. M. Grempe, *Teer u. Bitumen,* 27, 383 (1929).

can be increased considerably if heated to temperatures above those used in running. For example, a pontianak resin when heated to car-

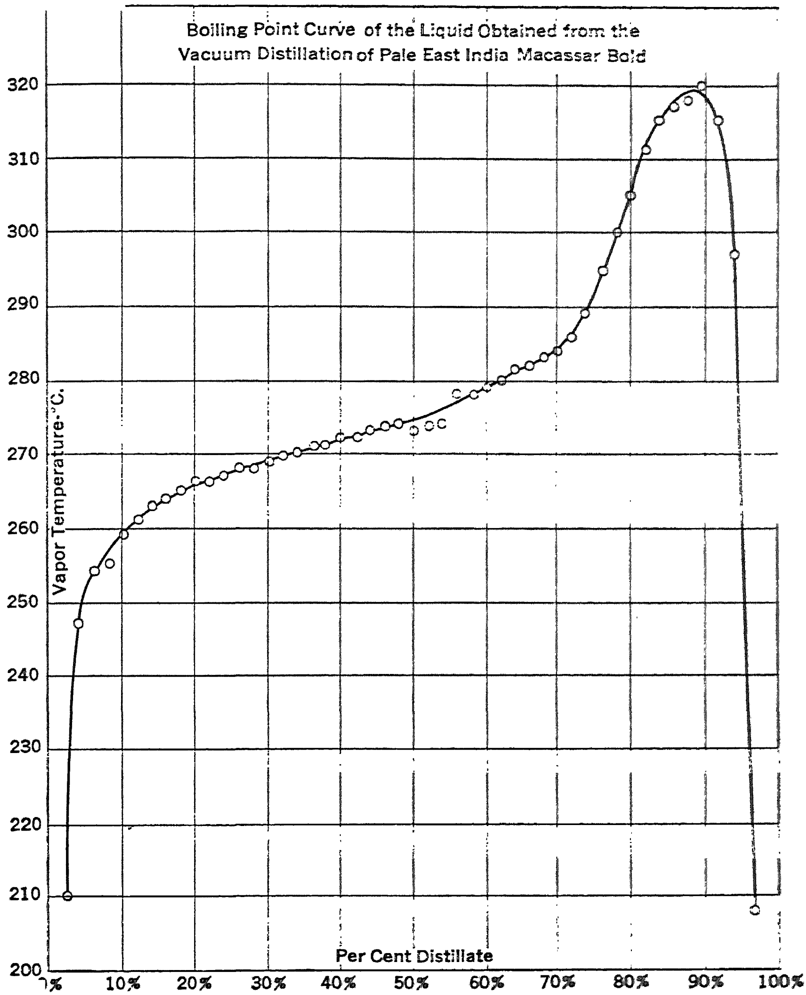


FIG. 47.

bonization yielded a liquid distillate corresponding to 77.2 per cent of the original resin weight. The carbonization point exceeded 400°C.

Powell has patented a process[39] for the destructive distillation of

[39] R. E. Powell, British Patent 480,436 (1938).

copals and damars in the presence of basic materials to yield liquid distillates of claimed commercial value. Calcium oxide, calcium carbonate, potassium carbonate, sodium carbonate, sodium hydroxide, and potassium hydroxide are the materials specified. The distillation is carried out at from 400 to 700°C. The mixture, it is stated, may carbonize. The more volatile products are recovered by adsorption with activated carbon, silica gel, or a suitable liquid. The distillate may be redistilled or otherwise refined to yield fractions assertedly suitable as lubricating oil, fuel oil, and gasoline substitutes, or as intermediates for the manufacture of alcohols, halohydrins, alkylolamines, and so forth. One particular application is as a collecting agent in flotation processes for sulfide minerals or minerals containing free copper, silver, or gold.

SUPPLEMENTARY REFERENCES

H. Wolff, "The Copal Melting Process," *Farben-Ztg.*, **29**, 2039-41 (1924).

A. Bergmann, "The Fusion of Copals in Large Quantities," *Peintures, pigments, vernis*, **8**, 1472-4 (1931).

Meister, "The Running of Copals," *Farben-Ztg.*, **37**, 1604-6 (1932).

R. Oda, "The Fusion of Copal," *J. Soc. Chem. Ind.*, Japan, **35**, suppl. binding, 106-7 (1932).

E. Stock, "A Practical Aid to Gum-Running," *Farben-Ztg.*, **37**, 484-5 (1932).

G. Dantlo, "Oil of Copal," *Peintures, pigments, vernis*, **10**, 6-7 (1933).

J. Breton, "Preliminary Mastication of Copals," *Rev. gén. mat. plastiques*, **12**, 71, 73 (1936).

E. J. Fischer, "Modern Methods for Purifying and Processing Natural Resins," *Farbe u. Lack*, 1936, 209-10, 219-20.

E. Mertens, L. Hellinckx, and C. de Hoffmann, "Catalytic Hydrogenation of Congo," *Bull. soc. chim. Belg.*, **45**, 637 (1936).

J. Breton, "Premastication of Copal Resins," *Rev. gén. mat. plastiques*, **15**, 107-9 (1939).

E. Mertens, L. Hellinckx, and C. de Hoffmann, "Hydrogenation Cracking of Congo Copal," *Bull. soc. chim. Belg.*, **48**, 1-11 (1939).

CHAPTER XVI

CHEMICAL MODIFICATION

Chemical modification of the natural resins has taken many forms. Many of the products obtained are of no commercial importance, some have potentialities, others are of commercial value.

Esterification of Copals. All natural resins contain resin acids. By esterification with polyhydric alcohols or fatty acid glycerides, products are obtained with improved gloss, durability, drying power, pigment compatibility, and flowing properties. In the preparation of cooked oil varnishes, the reaction between the acids present in the copals and the glycerides of the oil yield the improved qualities recognized in a properly bodied varnish.

The esterification of copals parallels the preparation of ester gum, but if certain precautions are not taken there is the danger of obtaining an infusible, insoluble, rubbery product. A mixture of copal and glycerin, carelessly heated, will usually result in the formation of a worthless mass of complex chainlike compounds owing to the condensation of high molecular weight esters. Products can be made which do not have all their reacting groups mutually esterified. Such an ester would not be compatible with basic pigments. Substantially complete esterification of the carboxyl groups before reaching the infusible stage is possible if a monobasic acid is heated with the resin and glycerin. If the resin is properly run, infusibility can be avoided without the use of monobasic acids. The esterification of copals with glycerin proceeds faster than that of rosin and can be conducted without the use of a catalyst.

Schaal in 1884[1] proposed esterification of copal with either phenol, cresol, resorcinol, or naphthol by heating at 180 to 210°C. The resulting resins were said to be usable in quick-drying varnishes.

Schaal proposed that copal resins, mixed with acid resins of conifers, such as colophony, or with acid mineral resins or with resin acids such as those produced by the oxidation of petroleum or of hydrocarbons from coal, be esterified with alcohols and hydroxyl derivatives, the most important of which were found to be glycerin, resorcin, mannite,

[1] E. Schaal, British Patent 12,807 (1884); German Patents 75,119 (1890); 75,126 (1891).

phenol, and cresols. When phenols and cresols were used, the addition of 25 to 50 per cent of glycerin and ½ to 2 per cent of boric acid was of advantage. Schaal[2] gave an example as follows:

To 50 lb. of previously melted Manila copal add 50 lb. of colophony and raise the temperature to 180 to 210°C. Add gradually a mixture of 6 lb. of fruit sugar and 6 lb. of glycerin under agitation, raise the temperature gradually to 280°C., and at the same time, by maintaining a vacuum of about 10 cm., draw off the aqueous vapors as they are produced, as the formation of resin and acid ester progresses. During the process of heating to 280°C., the alcohols which distil off are replaced by the introduction of fresh alcohols, until the formation of ester is complete.

In place of a mixture of 6 lb. of fruit sugar and 6 lb. of glycerin, a mixture of 16 lb. of phenol with 4 lb. of cane sugar or mannite and 4 to 5 lb. of glycerin, to which may be added about ½ lb. of boric acid, may be used.

H. Terrisse[3] claimed that fossil resins can be esterified after having been subjected to a depolymerizing or solubilizing treatment whereby they are rendered soluble in linseed oil or other siccative oils. The resin acids present will then combine directly and permanently with glycerin and other high-boiling alcohols and form esters.

The "depolymerization" process may be carried out in the presence of a solvent such as phenol, cresol, copal oil, resin oil, linseed oil, and the temperature is in general between 240 and 360°C. The solvent may be removed by distillation. The free acid value of the resin is determined and more than enough glycerin is added to neutralize the acids.

H. Terrisse[4] reported that when solubilized fossil resins are heated with glycerin or other high-boiling alcohols to their boiling points, the acids of the fossil resins are converted into stable neutral compounds, which are probably esters of the resin acids. These products are dissolved in oils and solvents, producing varnishes which are free from thickening or livering when used with basic pigments.

Ellis[5] described the esterification of natural resins. Congo copal was distilled at 315 to 325°C. for about 3½ hours. About 12 to 15 per cent of the oily distillate was collected. The resin was found to be completely soluble in benzol and the acid number was 88. One-sixteenth by weight of glycerin was added at 150°C. A reflux condenser was employed and

[2] U. S. Patent 501,446 (July 11, 1893).
[3] U. S. Patent 1,236,996 (Aug. 14, 1917).
[4] U. S. Patent 1,214,611 (Feb. 6, 1917).
[5] C. Ellis, U. S. Patent 1,242,161 (Oct. 9, 1917).

the mixture heated to 280°C. under constant stirring and in contact with aluminum. After a short time the mass was converted to a spongy product which solidified on cooling. It was very hard, not soluble in benzol and darker in color than the original congo. It was heated to slightly above 360°C. for a time, when the acid number was found to be about 20.

Varnish products for "enameling" the interior of tin cans used for preserving fruits and vegetables may be prepared from Congo copal ester.

Manila copal, kauri, pontianak may be esterified in a similar way, as well as mixed esters with rosin.

Ellis and Rabinovitz[6] reported that a sample of congo, run at 327°C. until soluble in turpentine, reacted vigorously upon the addition of glycerin to yield a spongy mass which could not be melted on heating to over 360°C. With similar apparatus to that which they used for congo, Ellis and Rabinovitz esterified damar and pontianak.

Ellis and Weber[7] state that in making the esters of fossil resins such as that of pontianak, manila, and congo, the fossil resin may first be treated with lime or other basic material capable of forming a resinate and the latter then treated with glycerin to produce the complex desired. A more desirable complex, however, is obtained by using a mixture of copal and rosin. For example, 4 or 5 parts of congo with 1 or 2 parts of ordinary rosin are melted and heated at about 300 to 310°C. in order to convert the congo into a soluble fusible product. Glycerin is introduced and the reaction allowed to proceed until the acid number drops to about 10.

If congo is fused with 10 per cent or more of rosin, the process goes on smoothly and agitation may be used advantageously. This combination is in condition for treatment with glycerin to form the complex desired; namely, the congo resin and rosin compound of glycerin, or, on the other hand, the congo and rosin, lime resinate or other resinate complex with glycerin. The temperature is about 290°C.

A modification of this method is that of first preparing a bath of molten rosin in a covered vessel having a vent for the escape of vapors. The rosin bath is heated to 300°C. and Congo resin is added gradually with stirring to form a solution of the congo in the rosin. A light-colored resin combination may be secured which is suited to form a complex with glycerin.

In place of rosin, it is possible to use a previously run fossil resin.

[6] C. Ellis and L. Rabinovitz, *J. Ind. Eng. Chem.*, **8**, 406 (1916).

[7] C. Ellis and H. M. Weber, U. S. Patent 1,381,863 (June 14, 1921).

The complex may be dissolved in oils and thinners to form varnishes which do not harden or liver in an objectionable manner when mixed with basic pigments.

Gardner and Holdt[8] determined the conditions under which polymerization occurs. The possible catalytic effect of metals was eliminated by using glass apparatus. They heated a Congo resin to 315°C. and held it at that temperature for 30 minutes. The resin appeared to be thoroughly run. When the temperature had dropped to 280°C., 10 per cent of glycerin was added and the temperature increased to 290°C. to combine the resin acids with glycerin. After 30 minutes the mixture became thick and gummy, then almost solid, and finally swelled to such an extent that the vessel was almost filled. The product was spongy and porous. Attempts at polymerizing congo in the absence of glycerin by heating for extended periods were failures. Gardner and Holdt showed that polymerization could be avoided if running were complete before the addition of glycerin. In this manner a sample of Congo copal was successfully esterified with 10 per cent of glycerin after first being heated for 90 minutes at 280°C. The excess of glycerin was apparent in the cold solidified resin. (Free glycerin lowers the moisture resistance and should always be removed. In commercial practice the excess glycerin is removed by vacuum distillation.) Hellinckx[9] has stated that, in order to obtain a non-reactive congo ester, the running should be continued until the acid number of the run resin has been reduced to 60 per cent of its original value, as congo when run to an acid number of only 70 per cent of its original value (sufficient to produce oil solubility) gelates upon esterification. The same author reports that the hydroxy constituents of Congo copal are non-reactive.

Gardner and Holdt[10] concluded from their experiments that incompletely run copals contain substances which must be changed or volatilized by heat if gelation is to be avoided.

Starting with a run Congo copal (acid value of 80) which had been run for 75 minutes, Gardner and Holdt added 6 per cent of glycerin and maintained the temperature at 280°C. The progress of the esterification was followed by acid number determinations and is recorded in Table LVII. Esterification takes place rapidly at the outset, for the

[8] H. A. Gardner and P. C. Holdt, *Paint Mfrs. Assoc. Tech. Circ. No.* 151, 269-78 (1922).

[9] L. Hellinckx, *Paint Manuf.*, 9, No. 9, 280-3 (1939).

[10] H. A. Gardner and P. C. Holdt, *Paint Mfrs. Assoc. Tech. Circ. No.* 151, 269-78 (1922).

acid value is almost halved during the first 10 minutes. The reduction becomes progressively slower thereafter. Catalysts and excess glycerin serve to hasten the esterification of copals. Zinc and aluminum are suggested catalysts.

Gardner and Holdt recommended the following procedure for the esterification of Congo copals: (1) Bring the resin to 315 to 325°C. quickly and hold there for 75 to 90 minutes or longer. (2) Lower temperature to 280°C. and add glycerin in slight excess (6 to 8 per cent). (3) Raise temperature to 292 to 295°C. and maintain until the desired degree of neutralization has been attained.

TABLE LVII

PROGRESS OF ESTERIFICATION OF CONGO COPAL

Time of Heating with Glycerin	Observations	Acid Number
10 minutes	Much glycerin left uncombined. Product cloudy	42
20 minutes	Some glycerin left uncombined. Product somewhat cloudy	36
30 minutes	Few drops of glycerin on side of flask at end of heating. Product clear	30
40 minutes	Product clear	23
50 minutes	Product clear	19
1 hour	Product clear	15
2 hours	Product clear but quite dark	5.5

Asser and Ruth[11] prepared oil-soluble, hard, and resistant compositions containing fossil resins by dissolving the latter in hot organic acid (linseed oil or tall oil, fatty acids, resin acids, etc.) at temperatures less than the decomposition temperature of the resin (200 to 250°C.) and then esterifying with a polyhydric alcohol (glycerin). Dissolution of the resin is facilitated by mixing the powdered resin with acid and gently warming (thus causing swelling) prior to adding the remaining acid.

Hocker[12] formed a glyceride of Congo copal in the following manner: Two or more parts of high-boiling rosin oil are added to 1 part of Congo copal and the mixture heated at 275 to 300°C. for 2 hours or until the copal is entirely fused. One gallon of glycerin for each 14 lb. of Congo copal is added and the temperature maintained at 280 to

[11] E. Asser and G. Ruth, British Patent 486,923 (1938).

[12] C. D. Hocker, U. S. Patent 1,638,579 (August 9, 1927).

300°C. for about 1 hour. After heating, the mass will contain uncombined copal. Treatment with glycerin is repeated until the acid number of the resin is reduced to about 10. The ratio of rosin oil to the copal should be not less than 2 to 1.

In another example, 3 parts of Congo copal are fused with 2 parts of tung oil fatty acids. Glycerin to neutralize both the resin and fatty acid is then added and the mixture heated, preferably in the presence of rosin oil. Some tung oil is formed and is polymerized.

Humphrey[13] patented the treatment of resin acids such as abietic acid, pimaric acid in pure or relatively pure state or as present in rosin, sandarac, pontianak, etc., with such esterifying agents as dichloroethyl ether, chloromethyl ether, *s*-dichloromethyl ether, for the production of various resin acid esters. In carrying out the treatment, various alkalies as, for example, sodium hydroxide, sodium carbonate, calcium carbonate, potassium hydroxide and the like may be used, and such alcohols as ethyl, amyl, isopropyl, butyl will be found satisfactory as solvents.

In Brendel's[14] method, copal was run until foam-free, after which the temperature was reduced to 150 to 200°C., the glycerin added, and the temperature slowly raised to 220°C.

Pearce, Carlson, and Rydstrom,[15] in preparing the esters of congo and manila, noted that the tendency to gelatinize was much more marked in the Manila resins. When incompletely run, the Manila resins polymerized to useless masses. Under the same conditions, Congo resins yielded soluble esters, although they, too, solidified during earlier portions of the reaction. When both the Congo and Manila resins were run to 25 per cent losses, soluble esters were obtained without intermediate solidification.

The ready polymerization of Manila resins upon heating with glycerin suggests their possible use in the preparation of thermosetting molding resins. In such an application, the molding resin could be prepared by heating a mixture of manila and glycerin to a temperature below that necessary for polymerization.

In modern copal esterification, the first operation is the running of the resin in closed vessels of special design (Fig. 48). These are equipped with mechanical and steam agitation, and provision is made for maintenance of an inert gaseous blanket (usually carbon dioxide)

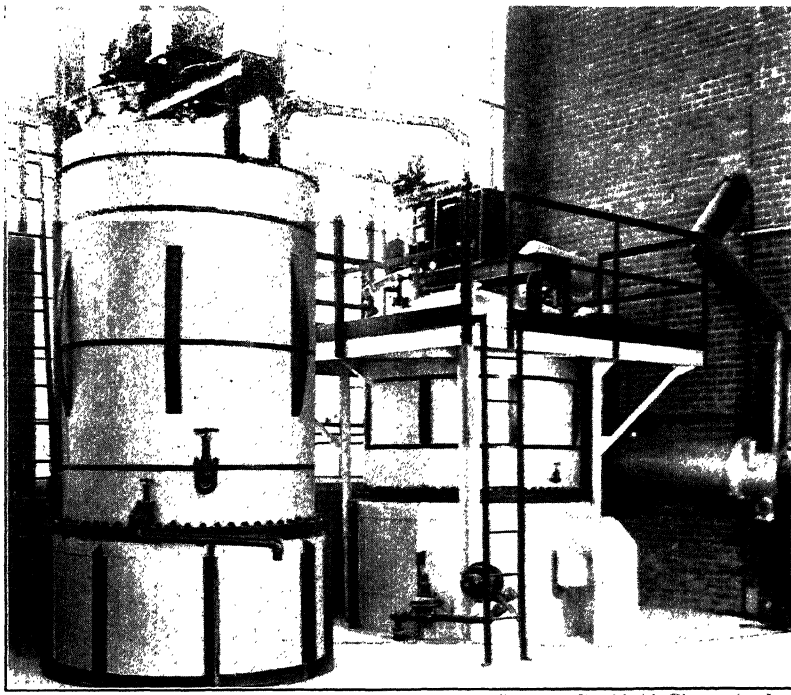
[13] I. W. Humphrey, U. S. Patent 1,843,284 (Feb. 2, 1932).

[14] H. Brendel, *Farbe u. Lack,* 31, 297-8, 310 (1926).

[15] W. T. Pearce, R. Carlson, and C. L. Rydstrom, *Ind. Eng. Chem.,* 19, 285-6 (1927).

over the resin charge. To avoid excessive darkening of the product, the heating surface is as large as possible. The burners are usually oil- or gas-fired.

Bergmann[16] described a German plant for esterifying copal resins in which 400 to 4,000 kilos of copal are treated in one operation to pro-



Courtesy Reichhold Chemicals, Inc.

FIG. 48. Modification of Congo resins.
Right: Kettle for fusing, esterifying, and modifying.
Left: Tank for blending individual batches.

duce 1,200 to 12,000 kilos of varnish. The whole process is conducted in an atmosphere of carbon dioxide.

In order to minimize fume loss in the running and esterification of natural resins, Frenkel[17] suggested the use of an apparatus heated indirectly with a high-boiling liquid medium (a mixture of phenyl ether and diphenyl) circulated through jacketed kettles. To obtain a good quality ester, an aluminum vessel is employed and an inert atmosphere

[16] A. Bergmann, *Peintures, pigments, vernis*, 8, 1472 (1931).
[17] H. L. Frenkel, British Patent 419,952 (1933).

is maintained. After the resin has been run to a satisfactory degree, a calculated amount of glycerin is admitted slowly. The mass is tested periodically until the desired acid value has been reached. When the acid value falls between 5 and 10, the reaction is stopped and any excess glycerin distilled off. An ester of this acid value has been found to have the best varnish-making properties.

During esterification, the water formed is removed as steam through a reflux condenser, while any volatilized glycerin is condensed and returned to the reaction.

American practice uses one or more of the following operations in the preparation of fused, esterified, and modified copals:

1. Mechanical pressure treatment (mastication).
2. Melting or running in apparatus specially designed to avoid overheating.
3. Neutralization, particularly by esterification with glycerin.
4. Chemical and mechanical bleaching.
5. Modification with rosin and natural and synthetic resins.

Congo esters are on the market in two forms: (*a*) pure congo-glycerin esters containing no flux, and (*b*) congo esters modified with rosin, ester gum, or a special flux. These forms offer advantages over raw fossil resins. The fuel and labor costs of running fossil copals along with the material loss and the annoyance and danger of fumes, fire hazards, and danger to workmen are usually more than enough to outweigh the price difference between esterified and natural copals. Properties of American copal esters are given in Table LVIII.

TABLE LVIII

	Acid No.	Color*	Melting Range °F.	Specific Gravity
Congo ester *A*	10–15	D–E	185–200†	1.05–1.10
Congo ester *B*	5–10	H–I	221–230‡	1.1
Congo ester *C*	5–10	J–K	230–248‡	1.1

* U. S. Dept. of Agriculture Rosin Standards.
† Capillary tube method.
‡ Mercury method.

The fluxed material is more readily soluble than the flux-free grade, but not to a very important degree. An advantage of the 100 per cent grade is that the varnish manufacturer knows the composition of the resin and can add rosin or any other resins as he wishes.

The authors have examined four samples of congo esters originating in the United States and in Europe. Their properties as found are given in Table LIX. With the exception of the viscosity and the color, there

TABLE LIX

Physical and Chemical Properties of Congo Ester*

	A	*B*	*C*	*D*†
Per cent insoluble content using toluol	0.21	0.14	0.40	0.15
Per cent ash	0.04	0.03	0.14	0.04
Insoluble deposition test using toluol				
cc.	Traces	0.25	0.25	Traces
color	17	16–17	16	12
Softening point °C.	75	83	78	80
Melting point °C.	130	110–120	128	108
Direct acid number	2.5	2.0	5.8	3.9
Saponification number‡	9.2	8.3	12.0	9.2
Iodine number	63	65	58	84

* All tests were run in duplicate. Figures are average values.

† *D* contained ester gum.

‡ After refluxing for 45 minutes, congo esters are difficult to saponify and for complete saponification it would be necessary to reflux for 22 to 30 hours.

was not much variance in the properties of the four different congo esters. The varying viscosity and color are due to differences in the severity of the thermal treatment encountered in their manufacture and perhaps to differences in the original Congo copal.

Solubilities in representative solvents were also determined. These are listed in Table LX.

Congo esters in nitrocellulose lacquers (containing equal parts of nitrocellulose and congo ester) require toluol or other coal-tar solvents to obtain clear solutions and films.

Properties of Copal Esters. The most marked improvement of copal esters over their original form is their compatibility with reactive pigments. Paints made by grinding properly prepared copal ester varnishes with basic pigments (zinc oxide, ocher) suffer no adverse thickening effects or hard settlement of pigment.

Copal esters are completely soluble in petroleum, coal-tar, and terpenic solvents, butyl or higher alcohols and their corresponding esters and ethers, ketones, diacetone alcohol, mesityl oxide, benzyl alcohol,

TABLE LX

SOLUBILITIES, COLORS, AND VISCOSITIES OF CONGO ESTERS

(50 per cent solutions)

Solvent	*A*	*B*	*C*	*D*	
Ethyl acetate	Soluble 18 A−	Soluble 18+ E	Soluble 18 B	Soluble 14 A−	Solubility Color Viscosity
Toluol	Soluble 18 A−	Soluble 18+ B	Soluble 18 C	Soluble 14 A−	Solubility Color Viscosity
Sunoco spirits	Soluble 18 D	Soluble 18+ L	Soluble 18 P–Q	Soluble 14 G	Solubility Color Viscosity
Dioxane	Soluble 18+ D–E	Soluble 18+ S	Soluble 18+ O	Soluble 15 G	Solubility Color Viscosity
Solox	Swelled	Swelled	Swelled	Swelled	
Butanol	Swelled	Swelled	Swelled	Swelled	
Acetone	Swelled	Swelled	Swelled	Swelled	

dioxane, Cellosolve, and Cellosolve acetate. Because of their alcohol insolubility, congo esters are used in the form of oil or spirit varnishes and lacquers for application to those surfaces which are exposed to the solvent—bars, trays, table-tops, cellarettes, etc.

These esters are soluble in all varnish oils. They may be dissolved without previous melting by heating with the oils to approximately 500°F. Thus, the difficulties of copal running are eliminated.

Copal ester varnishes are of greater consistency than comparable ester gum varnishes. Linseed oil bodies more quickly when cooked with copal ester than with ester gum or ordinary copal.

The neutralized fossil resin improves the drying time of oil varnishes, especially those made with linseed oil. The quantity of China wood oil in long oil length varnishes may be reduced to a minimum. As esterified copal varnishes possess good drying power of their own, lesser amounts of driers are sufficient, which in turn favorably influ-

ences color, color-retention, durability, gloss-retention, and freedom from blooming. The varnishes are stable in storage.

Copal esters approach the condition of being more foolproof than any other varnish resin, natural or synthetic, because of their ability to endure temperatures up to 600°F. without danger of decomposition. On the other hand, a number of synthetic resins are liable to serious decomposition at temperatures of 550 to 575°F., temperatures not unusual in varnish making.

Copal ester varnishes are darker in color than those prepared from other resins. Although these varnishes are darker in solution form, the difference is not maintained in their dried films. In phenolic resins, the apparent color difference between the two types of resin is quite deceiving, for after drying, a phenolic resin varnish film darkens while a copal varnish film bleaches.

Films of copal ester varnishes or lacquers impart no odor or taste to aqueous solutions with which they may come in contact. Krumbhaar[18] reports that copal ester varnish films when boiled in a 10 per cent sugar solution containing 0.5 per cent citric acid caused no spoilage of the liquid. In the same test, phenolic resin varnishes usually impart a bitter taste or an unpleasant odor. As phenol compounds are toxic, their presence as a component of a varnish film exposed to the action of fruits, preserves, jellies, etc., is undesirable. Copal esters are non-toxic and are a preferred material for all clear and pigmented films which come in contact with food materials, particularly as a varnish for coating the inside of food containers, beer kegs, etc. The inertness of copal ester films is important for those canned foods which are very sensitive to taste and odor, for example, peaches, pears, pineapple, strawberries.

Copal ester films are also more resistant to the action of alkalies. Alkaline solutions which whiten an ordinary congo film do not attack copal ester films.

Copal esters are favored for varnishes and enamels which are baked at temperatures in excess of 300°F. At such temperatures many synthetic resins suffer loss in gloss, adhesion, toughness, elasticity, and color. In contrast, copal esters usually develop these properties to the fullest at the higher baking temperatures. Copal esters are satisfactory for finishes which are exposed to elevated temperatures when in use, for example, as radiator enamels, insulating varnishes.

The solubility of copal esters permits their use in "cold-process"

[18] W. Krumbhaar, *Paint, Oil Chem. Rev.*, April 19, 1939, pp. 8-10.

varnishes where the resin is dissolved in a thinner, followed by the addition of oil and driers. Such varnishes show good brushing properties, adhesion, durability, weather resistance, and no yellowing. This method of preparation can be used by manufacturers who lack the facilities for varnish cooking. Such varnishes are inferior to a cooked varnish of the same formula.

Copal esters are not oxidized in solution, in contrast to some synthetic resins which may become insoluble through oxidation. They can be added to ester gum, alkyds, and phenolic resins to improve gloss, adhesion, toughness, and elasticity without imparting any bad effects. Synthetic resins, copal esters, and other natural resins possess separate advantages and these must be considered in formulating.

The properties of copal ester varnishes may be attributed to large molecular combinations between the copal and fatty acid glycerides. Such complexes may be responsible for the toughness and lack of brittleness of copal ester varnish films, apparent when the films are baked at high temperatures.

Wiles[19] conducted exposure tests on three types of congo esters: 100 per cent congo-glycerin esters, congo esters modified with rosin or ester gum, and congo esters modified with a flux other than rosin or ester gum. After a month's exposure, conflicting results were obtained with each of the 100 per cent esters when the maximum amounts of tung oil were incorporated in each varnish. Gloss retention was erratic and Wiles found it impossible to generalize on whether or not 100 per cent congo esters give the best results with a maximum of tung oil. In no instance was there any breakdown of the film. In the other classes, all films again remained intact. The esters of the second class, modified with ester gum, gave the best gloss retention with a maximum of tung oil. Those of the third class, containing a special flux, lost practically all their gloss with tung oil, but were comparatively good in a linseed-stand oil vehicle.

Copal Esters in Lacquers. The early samples of esterified copals were not satisfactory materials for use in nitrocellulose lacquers. Improvements in processing have produced copal esters possessing good solubility, stability, and compatibility. Lacquers prepared with copal esters and nitrocellulose have a number of advantages over those using other resins. The resin, behaving as an oil film after the evaporation of solvents, produces a finish which is tough, durable, has good gloss, and is resistant to water and dilute acids. Since the films are quite heat-

[19] W. H. Wiles, *Paint Manuf.*, 6, 108, 316 (1936).

resistant they are useful for tray or table lacquers, as hot dishes were found to have no effect upon them.[20]

Esterification of Copals with High-Boiling Esters. The method of heating resins with high-boiling esters has been used by a number of investigators. The process consists of heating the copal with an ester boiling about 200°C. and containing an acidic portion which can be volatilized. The process eliminates running the resin before esterification.

Hesse[21] prepared copal esters by using alkyl and aryl esters of phthalic acid. Equal parts of copal and diethyl phthalate were heated together and the lower-boiling products removed by distillation. Other esters possessing individual properties have also been proposed. Benzyl acetate or dibutyl phthalate can be heated with a copal at 300°C. for 4 hours to form the esters, with the acetic or phthalic acids being driven off as formed. The copal benzyl ester had a melting point of 43 to 52°C., an acid number of 20.6, and a saponification number of 105. Fonrobert and Lemmer[22] obtained congo benzyl ester, congo glycerin ester, kauri benzyl ester, and manila butyl ester. The preparation of the congo glycerin ester is reported as follows: 250 parts of congo is heated with 147 parts of stearic triglyceride for 4 hours at 300°C. The copal melts without excessive frothing and at 275°C. a calm-boiling melt is obtained. The stearic acid formed during the reaction is removed at the end of the esterification by heating at 260°C. under a 10-mm. vacuum. The product yield was 233 parts of ester (58.7 per cent yield) having an acid number of 1.5.

Esterification of Kauri. Because kauri resins are of a higher price than equivalent grades of congo, the former are seldom used in the preparation of copal esters. Occasionally, blends of congo-kauri esters are used[23] in electrical insulation varnishes. Varnishes made from kauri esters are tough, durable, have good gloss and adhesion, and show good weather resistance. Kauri esters are easily soluble in oils, ester solvents, and hydrocarbons. The ester produces a more viscous solution in oils than does the similar ester of congo.

Esterification of Damar. Principally because of their low acid numbers, damars have received scant attention in this field. Brendel[24] reported that the tackiness of ordinary damar varnish films could be over-

[20] M. Cochran, *Oil Colour Trades J.*, **89**, 1414-21 (1936).
[21] A. Hesse, U. S. Patent 1,003,741 (1911); German Patent 227,667 (1909).
[22] E. Fonrobert and F. Lemmer, U. S. Patent 1,952,367 (1934).
[23] M. Cochran, *Oil Colour Trades J.*, **89**, 1414-21 (1936).
[24] H. Brendel, *Farben-Ztg.*, **29**, 1693-4 (1924).

come by neutralization of the acidic constituents of the resin with glycerin. Two per cent of glycerin was recommended as satisfactory. Esterification was carried out at 180 to 270°C. in a manner similar to that followed in ester gum preparation. The product was free from tackiness and brittleness and could be used for outdoor work. Increasing the percentage of glycerin to 8 per cent produced poor results.

Acetocopal. Acetylation of Congo copals has been performed by Mertens and Hellinckx[25] who designated their product "acetocopal." Under proper conditions a product having the following constants is obtained, which is suitable for varnish manufacture or as a plasticizer:

Melting point	66°C.
Softening point	34.7°C. (Kramer-Sarnow)
Density $^{15}_{4}$	1.03900
Density $^{100}_{4}$	0.99683
Acid value	121
Saponification value	251
Iodine value	129
Index of refraction $^{20}_{D}$	1.5267

The formula $C_{21}H_{32}COOHOCOCH_3$, which corresponds to Tschirch and Engel's formula for the hydroxy acids of Congo copal, was reported for the compound.

Acetylation of Damar. An alkali-resistant product, acetylated damar, was made when 100 grams of Batavia damar E were heated with 100 grams of acetic anhydride and 200 grams of acetic acid over a steam bath and stirred continuously for 3½ hours. Undissolved solids were permitted to settle and the solution decanted into water. The acetylated damar precipitated and at this point was soft at room temperature. The water was poured off and clean water and solid sodium hydroxide added. Upon raising the solution to its boiling point, the acetylated damar melted, but did not dissolve. Additional solid sodium hydroxide, added until the solution was very strong, caused no attack. On cooling, the product was a brown, opaque solid which was hard at room temperature.

Butyrocopal. Congo copal has also been reacted with butyric acid by Mertens, Hellinckx, and de Hoffmann[26] to form a product known as "butyrocopal." This was prepared by heating 100 parts of ground congo with 50 parts of butyric acid under a reflux for 4 hours. The

[25] E. Mertens and L. Hellinckx, 15th Congr. chim. ind. (Brussels, September, 1935), 813-16 (1936).

[26] E. Mertens, L. Hellinckx, and C. de Hoffmann, *Bull. soc. chim. Belg.*, **46**, 253-5 (1937).

excess butyric acid was removed by distillation, leaving 110 parts of "butyrocopal" as a flexible, elastic, resinous mass. The color depends upon the quality of the copal used and is generally pale yellow. Other properties follow:

Melting point	117 to 118°C.
Softening point	70.5°C. (Nagel)
Density $^{20}_{4}$	1.025
Acid value	139
Saponification value	255.2 (6 hours)
Iodine value	97.8

Since the properties resemble those of acetocopal, similar uses for butyrocopal were foreseen by the investigators, notably in the varnish industry and as a plasticizer. Butyrocopal holds an advantage over the former in that it can be prepared with greater ease and with a greater yield.

Mixed Oil and Resin Esters. The glyceryl esters of drying oils are more reactive[27] with natural resins than they are with glycerin itself. The esterification of ester and resin takes place in theoretically calculated proportions, whereas the primary esterification of the oil usually demands a considerable excess of glycerin.

Glycerin esters of drying oil acids are solvents for all the spirit-soluble resins. On heat treatment, these solutions react to produce varnish materials.

Mundy[28] has classified the reaction products of resins and monoglycerides into two groups: first, those resins such as the run varnish resins, rosin, damars, and accroides which react in the proportions indicated from the calculation of acid value; and second, the unrun varnish resins (certain exceptions of which fall in the first group), and the spirit-soluble resins of which manila and shellac are examples.

Resins of the first group readily react with glyceryl esters to yield mixed esters of low acid value. The reaction is carried out under reflux. The speed of reaction can be increased by the use of reduced pressure. Both mono- and diglycerides may be used.

With run-Congo resins, the speed of reaction is rapid and almost neutral products are obtained. A congo-linseed ester is very stable and may be diluted with mineral spirits without precipitation. It has been claimed that harder and less depolymerized resins may be used than

[27] C. W. A. Mundy, *J. Oil Colour Chem. Assoc.*, 21, 96-109 (1938).

[28] *Loc. cit.*

are generally needed in the preparation of congo esters, with consequent improvement in certain properties.

The other type of reaction, in which the monoglyceride is used as a solvent for spirit-soluble resins and the mixed ester formed by heating the solution, cannot be satisfactorily performed if the two reactants are used in the theoretical proportions indicated by the acid value of the resin. With such proportions, gelation of the reacting mass is frequently encountered, because of secondary internal reactions and the lack of control of reaction speed. The resins can be dissolved in the monoglyceryl esters at low temperatures. Control may be attained by the addition to the reactants of such acidic materials as fatty acids or rosin, which increase solvent action.

Mixed oil-resin esters have given promising results in the field of baking finishes. The films are unaffected by water and possess great elasticity. Most of the work has been done with Congo copals. Encouraging results have been obtained with soft manilas, damar, and a number of other resins. Accroides has provided very interesting results, reacting in the calculated proportions to yield mixed esters. The water resistance of the film was claimed to be higher than any other varnish of similar oil length. The color of this product was very dark and therefore limits its use.

Brendel[29] proposed a mixed ester when he attempted to esterify copals in the presence of drying oils. The copals were run until foam-free, glycerin and linseed oil were added, and the whole mass was heated to 310°C. A related proposal was the use[30] of higher fatty acids with fossil resins and glycerin. In this patent, the resin is dissolved in the fatty acids and esterified with glycerin at 250 to 280°C. in an inert atmosphere.

Natural Resins in Alkyds. Incorporation of natural resins in mixed esters with glycerin or other polyhydric alcohols and dibasic acids was suggested by Arsem and others.[31] The proposals in this field have been numerous and only a few examples will be given.

Durr[32] claims that condensation of natural resins or resin esters with glyceryl-phthalate resins takes place above 200°C., the entire mixture becoming soluble in ethyl acetate. An example is as follows: To 100 g. rosin at 250°C. are added 100 g. Congo resin and 4 g. glycerin,

[29] H. Brendel, *Farben-Ztg.*, 29, 231 (1923).

[30] German Patent 575,199 (1933).

[31] W. C. Arsem, U. S. Patent 1,098,776, 1,098,777 (June 2, 1914); L. H. Friedburg, U. S. Patent 1,119,592 (Dec. 1, 1914).

[32] A. H. V. Durr, U. S. Patent 1,739,446 (1929); British Patent 303,386 (1927).

and the mixture is heated until limpid. The resin ester so made is then introduced at 170°C. into a product made from 200 g. glycerin and 285 g. phthalic anhydride, finally heating for 4 hours at 260°C. The final product is soluble in esters and mixed solvents.

A mixture of 285 parts phthalic anhydride and 200 parts damar is added to 240 parts of glycerin at 110°C., the temperature raised to 260°C. in 15 hours and maintained for 2 hours. The product has an Ubbelohde dropping point of 137 to 146°C.

A mixture of 200 parts phthalic anhydride and 200 parts Manila resin is introduced into 150 parts of glycerin at a temperature of 110°C. The temperature is raised to 170°C. in 5 hours and maintained at this temperature until the Manila resin is completely fused. The temperature is then raised progressively to 250°C. in 8 hours and the mass run off as soon as this temperature has been reached. The Ubbelohde dropping point of the product is 140 to 157°C. The acid number is 2 to 4.

Congo copal can be used to replace the rosin in the rosin-glyceryl-phthalate resins. The copal-alkyds are also compatible with nitrocellulose.[33] An example of copal incorporation into glyceryl-phthalate resins is as follows:[34] 45 parts stearic acid, 45 parts fused or run congo, 74 parts phthalic anhydride and 58 parts pentaerythritol are heated at 290°C. Resins from glycerin and polybasic acids modified with copal, kauri, damar, or resin acids may be used with a lesser proportion of cellulose ester for coating compositions.

Natural resins and alkyd combinations of these may be treated in inert solvents with volatile halides such as aluminum, titanium, or tin chlorides. Another modification consists of dissolving a natural resin in an aromatic hydrocarbon and treating the solution with aluminum chloride. The product can be incorporated in alkyd resins.[35]

Resins useful as cements for mica are made of Congo resin and a polybasic acid and polyhydric alcohol. By heating to 230°C. 1,000 g. of Congo copal, 247 g. phthalic anhydride, and 203 g. glycerin, a resin is obtained which may be either dissolved in benzol or toluol or mixed with a filler and molded.[36]

A binder for molding materials may be made by reacting glycerin with a natural resin such as rosin or a copal, and an acid such as

[33] H. M. Weber, U. S. Patent 1,757,104 (1930).

[34] C. Ellis, U. S. Patent 1,900,638 (1933); British Patent 327,095 (1928); French Patent 667,918 (1928).

[35] British Patent 399,206 (1932); 421,542 (1934); French Patent 734,525 (1932).

[36] T. F. Bradley, U. S. Patent 1,722,554 (1929).

phthalic, citric, tartaric, malic, maleic, or succinic. Diluents, softening or retarding agents may be incorporated with the binder.[37]

Natural resins of various kinds such as copal, manila, and damar may be used in conjunction with the various possible combinations of alkyd resins.[38]

Krumbhaar[39] described a resin made from a polyhydric alcohol, a reactive and soluble masticated congo containing a natural resinous hydroxy acid, a monobasic non-hydroxy carboxylic acid selected from fatty oil and resinous acids, and a polycarboxylic acid. These are caused to react together at a temperature below the fusing point for untreated copal.

Resin alcohols obtained from natural resin esters or acids (copals, sandarac, amber, tall oil) by catalytic or other reduction processes are condensed with organic or inorganic acids in the presence of a known esterification catalyst (boric acid) and/or other alcohols (glycerin).[40]

Preparation of an Alkyd Resin Using Batavia Damar. In an attempt to incorporate Batavia damar in alkyd resins as a raw material along with glycerin, phthalic anhydride, and fatty acids, the following mixture was refluxed at 320°F. for 7 hours:

Glycerin	25 g.
Phthalic anhydride	50 g.
Batavia damar A/E	300 g.
Linseed fatty acids	200 g.

The product was a homogeneous resin, dark brown in color, soluble in petroleum thinners, coal-tar solvents, and drying oils. The total loss in weight was 1 per cent.

Preparation of an Alkyd Resin Using Loba. The following mixture was refluxed:

Glycerin	25 g.
Phthalic anhydride	50 g.
Loba C	300 g.

At the end of 6 hours, the product was soluble in hot linseed fatty acids but not in oil.

The following mixture was refluxed at 360 to 380°F.:

Glycerin	25 g.
Phthalic anhydride	50 g.
Linseed fatty acids	100 g.
Loba C	300 g.

[37] C. Ellis, U. S. Patent 1,541,336 (1925).
[38] C. Ellis, U. S. Patent 2,000,937 (1935).
[39] W. Krumbhaar, U. S. Patent 2,110,803 (1938).
[40] Deuts. Hydrierwerke A.-G., British Patent 454,616 (1935).

At the end of 2½ hours, a homogeneous resin was obtained. The loss in weight was less than 1 per cent of the total original weight.

A test on a sample of the resin showed that it was insoluble in hot linseed oil. An additional 100 g. of linseed fatty acids when added to the product and refluxed for 10 minutes longer yielded a resin completely soluble in hot linseed oil. When used with China wood oil in the preparation of a varnish, the resin produced a film which dried in 8 hours. After a 24-hour drying period, a hard but very flexible film was obtained.

Preparation of an Alkyd Resin Using Elemi. An attempt was made to harden elemi by its incorporation as a constituent of an alkyd resin. The following weights of reactants were used:

Elemi	317.5 g.
Glycerin	23.0 g.
Phthalic anhydride	37.0 g.

These were refluxed for several hours at 300°F. No foaming was experienced. At the end of this period, the temperature was raised to 554°F. and the contents permitted to distil.

Throughout the heating, the color of the resin increased and became much darker than the original elemi. The final product was a clear, dark resin, much harder than elemi, somewhat tacky, and flexible. One possible use of the product obtained would be as a plasticizing resin. Its acid number was 19.3. Solubility tests, using equal parts of resin and solvent, showed it to be soluble in benzol, butanol, butyl acetate, Cellosolve, and largely soluble in mineral spirits. The viscosities of the first four solutions were less than 0.5 poise (A — on the Gardner-Holdt scale).

Elemi can also be hardened by distilling off most of its essential oils.

Chlorination of Soft Manilas. Experiments with manila MA and manila WS revealed the tendency of these resins to combine with chlorine. A small stream of chlorine gas was passed through a tube of finely ground resin. In the early stages the resin absorbed chlorine rapidly and was heated to 70 or 80°C. by the reaction. Weighings indicated the absorption to be complete at the end of 5 to 6 hours. The sample of MA absorbed 31 per cent of its weight of chlorine, the WS sample 20 per cent. Attempted distillation of the product proved the chlorine to be firmly combined with the resin. The products were much darkened and gave black solutions in alcohol. They were resinous solids melting at 125 and 124°C., respectively. Blackening appeared to be the only marked change in the resin's properties. Acid numbers were virtu-

ally unchanged. The chlorinated resin, like the original, was soluble in alcohol, and insoluble in benzol, petroleum naphtha, and hot linseed oil. As a spirit varnish, a hard but brittle film was obtained.

Albert and Berend[41] discovered that only when phenol and formaldehyde were reacted in the presence of rosin, balsam, or natural resins in quantities greater than required for their action as catalysts, was the product soluble in oils.

Berend made a resin which had a melting point of 135 to 165°C. and which was soluble in linseed oil, turpentine, or benzol, by refluxing 95 g. of carbolic acid with 70 g. of 40 per cent formaldehyde solution and 0.2 g. of hydrochloric acid to a temperature of 110 to 112°C. Thirty grams of Manila copal were added and the mixture refluxed for 6 hours. The water was removed and the resin mixture freed of volatile components by heating for 2 hours at 210°C.

Another resin, melting at 160 to 205°F. with the same solubility as fossil copals, was made by heating 108 g. of cresol, 30 g. of turpentine resin, and 28 g. of paraformaldehyde for 6 hours at 115 to 120°C. Fifty grams of kauri resin were added in small pieces and the whole heated while stirring. The water and volatile ingredients were removed by heating for 2 hours at 250°C.

Useful conversion products have been obtained by reacting natural resins and their esters with phenols in the presence of boron fluoride or hydrogen chloride.[42]

In modifying phenolic resins to obtain a satisfactory material for oil varnishes, fusion of the natural resin for 3 hours at 300°C. was necessary to accomplish this result.[43]

Seebach[44] combined natural resins such as rosin, damar, copal, mastic, shellac, accroides, with phenols containing more than one benzene ring or with phenols with more than one hydroxyl and one or more benzene rings. The advantageous action of natural resins on the formation of colloidal solutions of the condensation products in fatty oils and varnishes is unexpected and surprising.

[41] K. Albert and L. Berend, British Patent 1269 (1912); French Patent 441,547 (1912); German Patent 254,411 (1910); German Patent 269,659 (1911). L. Berend, U. S. Patent 1,191,390 (1916); German Patent 281,939 (1913). I. S. Melanoff, U. S. Patent 1,804,379 (1931).

[42] French Patent 734,390 (1932).

[43] L. Berend, U. S. Patent 1,205,081 (1916), British Patent 15,875 (1914); Swiss Patent 72,631 (1916); German Patent 289,968 (1914); German Patent 281,939 (1913).

[44] F. Seebach, U. S. Patent 1,844,824 (Feb. 9, 1932).

Melanoff[45] suggested a plastic from congo, phenol, aldehyde, and alkali.

Copals have been widely recommended as modifiers for varnish type phenol-formaldehyde resins.[46]

Miscellaneous Uses of Accroides. W. H. Wright[47] suggested a composition of 100 parts rosin, 100 parts accroides, and 10 parts glycerin, melted together under a sufficient temperature to make them fluid, as an oil-proof, grease-proof, waterproof coating which has insulating dielectric properties.

When accroides is treated with a hydroxypolymethylol benzene having at least two carbinol groups attached to the benzene nucleus, a resin results.[48]

Novotny[49] suggested accroides as a phenol resin modifier. Fifty parts by weight of phenol, 42.5 parts furfural, and 35 parts gum accroides are mixed and heated. The mixture is strained and 0.75 parts of potassium carbonate are added to the clear product. After refluxing or distilling, an end temperature of 200°C. is reached and a hard, brittle resin melting at 200°C. results.

Ninety parts of accroides in 650 parts of alcohol and 38 parts of 40° Baumé sodium hydroxide were heated to boiling and 106 parts of para-toluol-sulfonchloride were added. The neutral resin was soluble in benzol and butyl acetate but insoluble in alcohol and various petroleum distillates.[50]

[45] I. S. Melanoff, U. S. Patent 1,804,379 (May 5, 1931).

[46] M. Bottler, *Kunstoffe*, **17**, 149 (1927); W. Ebeling, *Farbe u. Lack*, **36**, 505 (1931); E. Fonrobert, *Kunstoffe*, **12**, 121 (1922); *Farben-Ztg.*, **35**, 1506, 1554, 1606, 1658 (1930); *Synthetic and Applied Finishes*, **5**, 249 (1935); *Paint Oil Chem. Rev.*, **88**, 17, 89 (1929); H. A. Gardner and G. G. Sward, *Am. Paint Varnish Mfrs. Assoc., Circular No. 410*, 129-34 (1932); A. W. C. Harrison, *Paint Manuf.*, **2**, 243, 251 (1932); H. Hebberling, *Kunstoffe*, **20**, 56 (1930); *Oberflachentech.*, **11**, 143 (1934); H. M. Johnson, *Paint, Oil Chem. Rev.*, **93**, (22), 10 (1932); C. P. A. Kappelmeier, *Chem. Weekblad*, **31**, 423 (1932); D. H. Killeffer, *Sci. Am.*, **145**, 238 (1931); E. Nierman, *Peintures, pigments, vernis*, **9**, 146, 163, 174 (1932); **10**, 8, 26, 38, 103 (1933); A. J. Norton, *Am. Paint J.*, **15**, (30), 22f. (1931); *Paint, Oil Chem. Rev.*, **96** [12], 13 (1934); O. Nouvel, *Allgem. Oel- u. Fett-Ztg.*, **28**, 188 (1931); H. W. Rowell, *J. Soc. Chem. Ind.*, **46**, 234 (1927); P. Snitter, *Bull. inst. pin*, 223 (1933); H. Ulrich, *Farben-Chem.*, **6**, 12 (1935); E. E. Walker, *Chem. Trade J.*, **88**, 330 (1931); *Times, Trade and Eng.*, **28** [664], 7 (1931); F. G. Weed, *Paint, Oil Chem. Rev.*, **91** [23], 12, 40 (1931); H. Wolff, W. Toeldte, and G. Seidler, *Farben-Ztg.*, **33**, 1724 (1928).

[47] U. S. Patent 1,833,810 (Nov. 24, 1931).

[48] General Plastics, U. S. Patent 2,186,406 (1940).

[49] E. E. Novotny, U. S. Patent 1,902,461 (1933).

[50] K. H. T. Pfister, U. S. Patent 1,608,421 (Nov. 23, 1926).

Cracked congo has been suggested for incorporation with methylol-urea,[51] and the naturals have been proposed as additions to urea-formaldehyde plastics,[52] to benzene and toluene sulfonamide aldehyde resins.[53]

Copal-creosote oil combinations give rubber-like masses[54] for erasers.

Scheiber[55] mixed Manila copal dissolved in alkali with an alkaline solution of a polyhydroxy-carboxylic aliphatic acid (trihydroxystearic acid, trihydroxypalmitic acid), and precipitated the resin by hydrochloric acid. After filtering and heating to 150°C., the resin is alcohol soluble and heat convertible.

SUPPLEMENTARY REFERENCES

K. Pfister, "The Inter-Esterification on Heating Fatty Acid Glycerides with Resin Acids," *Farbe u. Lack*, 1925, p. 456.

G. Dantlo, "Preparation of the Ester of Congo Gum," *Peintures, pigments, vernis*, 9, 23-4 (1932).

W. Krumbhaar, "Fundamentals of the Production and Use of Processed Fossil Gums," *Official Digest*, Federation Paint & Varnish Production Clubs, No. 134, 43-8 (1934).

A. Mann, "Rosin and Copal Esters," *Farbe u. Lack*, 1934, pp. 146, 158.

H. Kemner, "Congo Copal Esters, Their Production and Use," *Farbe u. Lack*, 1935, pp. 495-6.

H. Ulrich, "Esterified Copals and the Possibilities of Using Them in the Varnish Industry," *Farbe u. Lack*, 1935, pp. 135-6.

G. Dantlo, "Esterification of Congo in the Varnish Industry," *Compt. rend.*, 204, 365-6 (1937).

[51] C. Ellis, U. S. Patent 1,536,881 (1925).

[52] German Patent 569.342 (1927); British Patent 287,727 (1927).

[53] H. A. Gardner, U. S. Patent 1,564,664 (1925), British Patent 351,637 (1930); C. Dreyfus, British Patents 315,807 and 315,808, Canadian Patents 329,371 and 329,372 (1933).

[54] F. C. Zobel, U. S. Patent 1,786,281 (1930).

[55] J. Scheiber, U. S. Patent 1,938,468 (1933), 1,903,598 (1933); British Patent 350,764 (1929); German Patent 551,093 (1929).

CHAPTER XVII

PURIFICATION

In comparison with competitive materials, natural resins have always been at an initial disadvantage. With the exception of the surface cleaning performed on better grades of fossil resins, they have not been purified of their dirt and insoluble matter other than the purification incidental to the grading and sorting operations. The color of the lower grades is sometimes poor. When cut in solvents there usually is a small residue of dirt and gelatinous particles of a non-resinous character. The user must become a processor in order to secure the good features of natural resins. Large paint and varnish companies are prepared to do this, and do purify their resins, but the smaller companies frown on the extra expense. The unfortunate thing is that non-users believe the naturals to be dirtier than they actually are. Seldom are complaints directed at any of the inherent properties of the resin itself.

With processed natural resins on the market, uniformity of a single grade would be an improvement over the number of grades now existing, since even in one grade, different colored pieces are found. Non-uniformity does exist and constitutes a source of annoyance to some users.

An increasing number of small plants exist with limited capital and no extensive equipment. The product goes through the plant with a minimum of processing. The manufacturer can buy pretreated oils, pigments ground to new finenesses, pigments dispersed in oil or lacquer bases, alkyd resins that are varnishes in themselves, and specially prepared grinding vehicles. All his raw materials have been pretreated in a manner to relieve him of these processing steps. It would be possible in such a plant merely to mix the ingredients in a tank to secure a finished paint, varnish, or lacquer. Not all plants are as elementary as the one cited, but it illustrates the growing *compounding* rather than *manufacturing*. In the face of such a tendency, unprocessed natural resins are out of step with other raw materials. Untreated and processed resins are compared in Table LXI.

There are four main problems involved in the complete purification of natural resins:

1. Removal of such dirt as bark, twigs, and sand.

TABLE LXI

Disadvantages of an Untreated Natural Resin	Advantages of a Processed Natural Resin
1. In order to remove the dirt (woody and siliceous material) and the insoluble portion (gelatinous matter) of a natural resin, it is necessary for the consumer to process it. This involves extra expense through loss of time, loss of solvent, and the need for equipment.	1. A processed natural resin consists entirely of soluble resin. There is no dirt or insoluble matter present to bedevil the consumer.
2. As the resin contains dirt and insoluble matter, one pound of resin "as purchased" is not equivalent to a pound of actual resin.	2. A pound of processed natural resin contains one pound of actual resin. It is 100 per cent soluble.
3. The difference between the actual resin contents of different grades of the same resin can lead to poor results in certain formulae when an attempt is made to use a grade other than that specified in the original formula. This danger exists whenever the resin content is near its critical point (as in emulsions).	3. This danger will never be encountered when processed natural resins are used, for resins of 100 per cent actual resin content will be specified.
4. Damar resins before being used in nitrocellulose lacquers, must always be dewaxed by the lacquer manufacturer. The wax is never purified and placed on the market although a demand exists for it.	4. The damar wax, for which there is an ever growing demand, will also be purified.
5. At present a lack of uniformity sometimes exists within each grade and between different lots of the same grade.	5. By processing large batches of resin, variations would be ironed out.
6. There are too many grades for each type of resin.	6. Processing would decrease the number of grades on the market.
7. Some of the lower grades possess colors that would be too dark for certain uses.	7. By processing, it is hoped to remove most of this color.
8. Complaints are sometimes raised on the grounds of instability of certain natural resin solutions over a period of time. This is true particularly of batu, black and pale east indias. It is due to the separation of a cloud.	8. Processing would remove this cloud and thus prevent its later separation.

2. Removal of the insoluble portions of the resin (wax of damars and gelatinous matter of manilas).

3. Removal of cloudiness. This perhaps could be classed under 2.

4. Removal of color.

Cloudiness cannot be removed by mechanical equipment, except in dewaxed damar solutions. This cloudiness appears when the resin is dissolved and is evenly distributed. The cloud with damars will not settle out even after long standing whereas it will with manilas. Cloudy solutions deposit clear films. The amount of cloud depends on the solvent and its removal enables the consumer to sell crystal-clear solutions. Complete clarification may be attained by the use of chemicals. The color of most natural resins (once the dirt has been removed) is not poor enough to justify a decolorizing operation except for the lower grades.

Methods of purifying natural resins resolve themselves into three groups: (1) dry mechanical means; (2) wet (solvent) mechanical means; (3) solution methods involving settling, dewaxing, the use of clarifying and bleaching agents, and decolorizing.

1. Dry mechanical means. The dry resin is mechanically separated from its dirt (bark, twigs, and siliceous matter). No solvent is used. The resin is roughly separated into three products: one containing the heavy siliceous material and a small amount of resin, another containing resin with only a small amount of dirt, and the last containing most of the light woody contaminants and some resin. The separation cannot be complete, but it is a means of lightening the burden on the subsequent cleaning and decolorizing operations. This does not apply to method (*e*). (See below.)

Dry separation may be effected by (*a*) tabling, (*b*) electrostatic precipitation and separation, (*c*) air separation, (*d*) flotation, and (*e*) filtration of melted resin. With the exception of (*e*) these methods are worth while only for the poorer grades of resin which are of small particle size. For larger sizes preliminary grinding would be necessary. The large-sized resins are fairly free of dirt.

2. Wet (solvent) mechanical means. Here the resin is dissolved in a solvent and its insoluble matter separated from the solution. The commercially available apparatus are centrifuges, supercentrifuges, and filters.

3. Solution methods. These methods range from simple or accelerated settling to bleaching and decolorizing procedures similar to those used in the purification of rosin. Examples are (*a*) natural settling, (*b*) acceleration of natural settling by clarifying agents, (*c*) removal of

color by clay, (*d*) removal of color based on selective solvency by chemical compounds such as phenol, furfural, furfuryl alcohol, resorcinol, aniline, sulfur dioxide, and propane, following rosin purification methods, (*e*) processes similar to the bleaching of shellac, (*f*) dewaxing of damar resins by precipitation and extraction.

Dry Mechanical Means. *Tabling.* Resins can be purified by shaking tables supplemented by an updraft of air. Resin is fed onto a vibrating

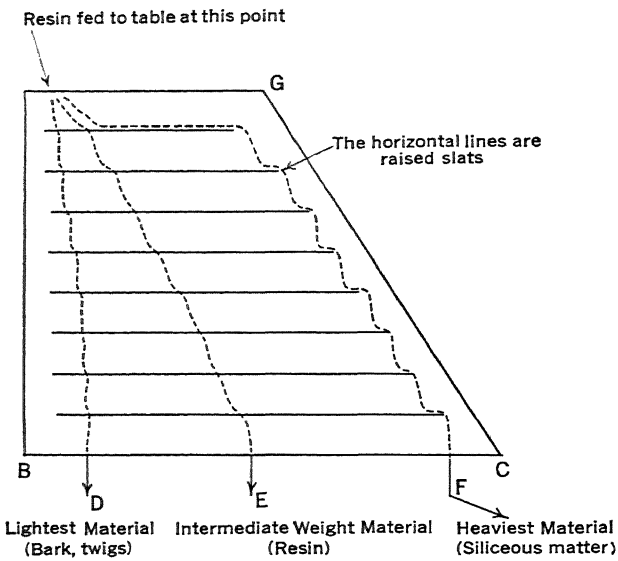


FIG. 49. Top view of the shaking table used in the investigation of resin purification.

table (Fig. 49) where three components (wood, resin, and siliceous material) owing to their differences in density will gravitate toward different sections of the opposite end (*BC*) of the table. The lightest material (bark and twigs) will come off nearest to the point of feed, whereas the heaviest component (siliceous material) will come off farthest away, from the feeding point. The resin, being of intermediate density, will come off at an intermediate point.

The impetus to each particle is given by a combination up-and-down and sidewise motion of the table. The up-sweeping air acts as a fluid to cause stratification of the three components. The downward flight is further aided by having sides *BC* and *CG* slightly lower than their corresponding sides *AG* and *AB*. Raised slats across the table surface make passage over them difficult for the heavier particles. The lighter

particles, because of their lesser inertia and also their buoyancy in the updraft of air that is continually passing up through the cloth surface of the table, negotiate the jump and can successively hop over these obstructions with a minimum of sidewise travel. The dotted line *AD* represents the approximate path of such a light particle.

A heavy material, such as a piece of sand, finds difficulty in hopping over these slats and consequently its travel will consist of a series of jerks along the slat toward the side of the table (*CG*) where the first slat ends. Here the piece of sand will fall from the first slat to the next one and will work along it until it reaches the end. There are particles of sand which, instead of taking the outlined path *AF*, will hop over the slats, but with so much lateral travel that by the time they have crossed all the slats they too come off at point *F*.

The resin, being of a density intermediate to that of the bark and sand, will take path *AE* with more lateral travel between each hop than is the case of the bark.

In operation, the table is covered with a pulsating mass of resin and the products fall off the table at end *BC*. Guide vanes placed along the end *BC* conduct the various cuts into bins below. The placement and number of these guide vanes is determined by the material at hand and by the degree of separation desired. Any dust raised by the air current in its passage can be reclaimed by the use of a dust-collecting device at the point of feed. It is not necessary to cover the table top completely.

The authors have investigated tabling of Batavia damar seeds and dust and loba dust. Better separation occurs if the feed is of a fairly uniform particle size. The resins were screened to separate the sample into portions, each of a fairly uniform particle size. Designation such as +20 means that this portion is retained on a 20-mesh Tyler standard screen. Similarly, −100 would mean that the portion passes completely through a 100-mesh screen. A portion with the designation −20+35 indicates that all of this resin passes through a 20-mesh screen but is retained on a 35-mesh screen.

The screened portions were tabled into four products. The character was always the same: product 1 contained the heavy siliceous matter; product 2 was the largest portion and represented the cleaned resin; product 3 contained woody matter; product 4 contained most of the woody material.

Table LXII gives the results on Batavia damar dust. Results of three test runs are summarized in Table LXIII.

Figure 50 permits tracing each pound of resin and each pound of

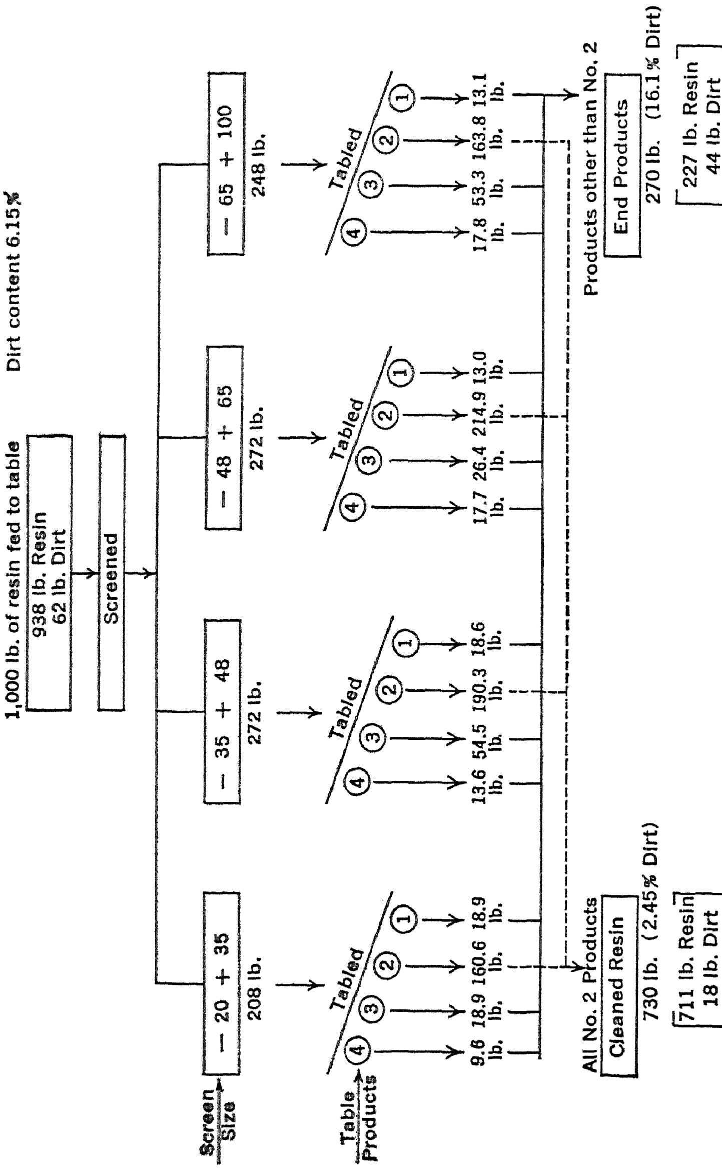


Fig. 50. Tabling of Batavia damar dust.

dirt for a typical tabling operation. The chart (Fig. 50) is based on figures in Table LXII.

TABLE LXII

INSOLUBLE CONTENTS OF TABLED PORTIONS OF BATAVIA DAMAR DUST

Screen Size	Product Number	Percentage of Original Sample	Per Cent Insoluble Content
−20 + 35	1	1.89	40.0
	2	16.06	3.00
	3	1.89	5.13
	4	0.96	16.9
−35 + 48	1	1.86	61.6
	2	19.03	2.19
	3	5.45	4.68
	4	1.36	14.4
−48 + 65	1	1.30	63.8
	2	21.49	2.30
	3	2.64	5.83
	4	1.77	8.98
−65 + 100	1	1.31	47.5
	2	16.38	2.39
	3	5.33	3.66
	4	1.78	4.83

TABLE LXIII

	Batavia Damar Seeds	Batavia Damar Dust	Loba Dust
Cleaned resin yield, per cent	93.7	73.0	70.8
End products, per cent	6.3	27.0	29.2
Original dirt content, per cent	3.01	6.15	12.2
Average dirt content of cleaned resin portions, per cent	1.79	2.45	7.00
Average dirt content of end products, per cent	21.0	16.1	25.6
Per cent removal of dirt*	44.7	71.0	59.5

* Per cent removal of dirt is that amount of original dirt which has been concentrated in the end products.

The advantage of preliminary separation over straight solution purification is that a lighter-colored product can be obtained. Dry separation concentrates most of the bark and twigs in one of the end products. Solvents extract natural coloring matter, such as tannins, from this woody material so that the solution assumes a reddish-brown cast. If a great deal of woody material is present (as in the lower grades), the solution will become quite dark. The resin contributes very little to the color of its solution. Almost all the dark color can be attributed to coloring matter within the impurities.

Installed cost of separating tables is from 75 cents to $1 per pound hourly capacity, while power requirements are 10 hp. per ton hourly capacity. The operating cost is about 350 lb. per kw.-hr.

Fineness of feed affects the efficiency of separation. About 20 to 65 mesh is the optimum range of particle size. On sizes smaller than 100 mesh, separation is not satisfactory. Particle size also determines capacity, as shown in Table LXIV.

TABLE LXIV

Damar Seeds		Damar Dust	
Size	Capacity, lb. per hr.	Size	Capacity, lb. per hr.
−10 + 20	2400	−28 + 48	1600
−20 + 35	2000	−48 + 100	1000
−35	1850	−100	800

No appreciable quantity of resin need be lost through end products, for these can be retabled until an economic limit is reached, whereupon the final fractions can be reclaimed by solvent methods if the resin contents warrant. Tabling can remove only the dirt that is mechanically held; the gelatinous or cloudy matter of the resin cannot be removed.

Tabling has applications (*a*) as the first step in the complete purification of natural resins, (*b*) as a means of bringing off-grade samples within specification limits or (*c*) improving present grades.

Electrostatic separation. Electrostatic and electromagnetic separation methods have been experimentally applied to congo, kauri, manila, and damar dusts without success.

Air separation. Air classification or air winnowing utilizes the differ-

ent settling rates of the components of the resin in a blast of air, which acts as a fluid. Each component is carried by the air a distance inversely proportional to its density. Tests have been conducted in the past but poor results were always obtained.

Flotation. Flotation is normally regarded as a wet process, inasmuch as water is used. The authors prefer to consider it a dry process, as no solvent is used and the resin remains unaffected by the water.

Although the possibility exists of using flotation methods in place of tabling, the authors were interested in it primarily as a means of recovering the resin from the end products of tabling. The third and fourth products obtained from the tabling operation contain the woody matter plus an appreciable percentage of resin. The woody material is between 15 and 25 per cent of the residue, the remainder being resin with perhaps a negligible trace of siliceous material. It is this resin that may be recovered through flotation. These end products can be retabled to effect further separation, but even then a residue is eventually obtained containing recoverable resin.

Flotation is based on the phenomenon that some materials are easily wet by water whereas others are not; or, to express it another way, gas bubbles attach themselves more readily to some materials and, when so attached, resist being displaced by water. Such particles are endowed with a false specific gravity and float to the surface whereas the particles of an easily wet material have no bubble layer and sink to the bottom.

This difference in floating ability may be accentuated by special conditions and flotation agents. The bubbles are usually generated by mechanical or pneumatic agitation and the particles are borne up on the resultant froth. Bubbles may be momentarily generated in pure water, but in order that they may last long enough to perform their work, some contaminant must be present to lower the surface tension of the water.

These contaminants are known as flotation agents and are chosen to meet the problem on hand. Some are used to stabilize the bubbles and others are used to aid in forming large quantities of froth. A few combine both properties. It is necessary to add only a small amount of agent. In the metallurgical industry (this was the origin of the flotation process), from 0.25 to 4 lb. is used per ton.

A flotation cell in its simplest form provides for the generation of bubbles, the overflow of the froth, and the withdrawal of the settled material.

Tests show that a flotation operation can be used on dust grades of

resin to produce a cleaner product with less loss of resin than is the case with tabling. However, a flotation process is more complex, needs more labor, and involves such additional operations as grinding, classifying, settling, filtering, and drying.

The following figures taken from a test run on Batavia damar dust (6.49 per cent insoluble) reveal the degree of purification possible with flotation:

Basis: 100 Tons of Original Resin

93.8 *tons of concentrate*

Assaying	Containing
2.53% insoluble	40.5% of the total insoluble matter
97.47% soluble	97.1% of the total soluble matter

6.2 *tons of tailings*

56.25% insoluble	59.5% of the total insoluble matter
43.75% soluble	2.9% of the total soluble matter

Filtration of melted resin. Melted resins can be purified by filtration. When heated to their melting point, resins begin to foam and the mass becomes filled with bubbles. This is not owing so much to decomposition as it is to the occluded air and the volatilization of moisture and other constituents. The high viscosity of the liquid resin and the lesser density of the woody impurities prevent the settling of the insoluble matter. Vacuum or pressure filtration is necessary.

A brass cylinder 8 in. long and 3 in. in diameter was fitted at one end with a threaded brass cap perforated by a number of small holes (3/16 in.), and immersed in a heated oil bath. With a fine brass screen placed in the bottom, the cylinder was filled with melted resin and pressure was applied by a weighted piston. The results are given in Table LXV.

TABLE LXV

Resin	Temperature, °C.	Pressure, lb.	Screen, Mesh per in.	Time, hrs.	Yield, g.	Per Cent Dirt		Melting Point, °C.
						Orig.	Final	
Damar seeds	140	30	140	1	276	3.35	Trace	97
Damar dust	150–160	70	275	1.5	175	4.14	Trace	90
Manila MA	180–200	100	140	3	85	3.63	Trace	112
Loba dust	180	100	140	1	50	25	3.3	120

The high temperatures increased the colors of the damars and manilas. The viscosities were unaffected, as were the acid numbers and the luster. The cleaned damars were of lower melting point and their films correspondingly more tacky. The melting points of the manilas were unchanged.

The pressure filtration of melted resin has commercial possibilities, but the design of apparatus should permit easy cleaning of the filter.

Wet Mechanical Means. *Centrifuging.* Centrifuging is an efficient method for "roughing out" insoluble matter in a resin solution. It is essentially a method of accelerated settling or gravity filtration wherein the force acting on the liquid is enormously increased by centrifugal force.

The machine can be either under-driven or suspended. The baskets are either perforated or imperforate. The perforated basket has a backing of coarse wire screening and a fine cloth or wire mesh filter. With this type of basket the centrifuge is an accelerated filter. The imperforate or solid basket has no perforations and no filtering medium. The solution passes over the top of the basket and into a collecting tank. With this type of basket the centrifuge is essentially an accelerated settling unit. Horizontal baffles are placed inside of the basket to lengthen the path of the effluent.

The wet solids retained in the solid basket will contain more solvent and resin solution than those retained in a perforated basket. The drainage is better in the latter type. The task of solvent and resin recovery from the wet solids is a greater problem in the case of the solid basket. Two runs were made on the same solution of loba dust in alcohol using a perforated and a solid basket.

TABLE LXVI

	Perforated	Imperforate
Per cent wet solids, based on original sample	8.5	17.4
Per cent effluent, based on original sample	83.0	74.7
Per cent loss, based on original sample	8.5	7.9

On the same size machines, the throughput is less for the solid type. A perforated basket may clog up and be undesirable for use with volatile solvents, inasmuch as evaporation at a perforation may produce solid resin that acts as a plug. The effluent from a solid basket is prone to carry over particles of light material. Some fines pass through 325

mesh screens. The wax in a dewaxed damar solution cannot be completely removed with a perforated basket. A solid basket gives complete clarification.

Under-driven centrifugals cannot be completely fume-proofed and cannot be employed with solvents. The suspended type can be equipped with self-discharging baskets, positive control, mechanical unloaders, fume-proof hoods, explosion-proof motors, and baskets in any machineable metal and all coatings.

For only one resin, dewaxed damar, could a crystal clear solution be obtained. Centrifuges clean the solution (with the exception of a very small amount of fines) but do not clarify it. Based on test data using 50 per cent manila and damar solutions, a throughput of 1,908 gal. per hour is indicated for a 40-in. centrifugal, and an average daily rate of 1,550 gal. per hour. Both throughputs include time lost in braking and cleaning. For example, it is estimated that the basket will be full of solids in 50 minutes after feeding 1,400 gal. Allowing 4 minutes for braking and cleaning, a total cycle would be 54 minutes for 1,400 gal., or 1,550 gal. per hour.

The operating cost is low, since power required is 4 kw.-hr. per ton per hour.

Supercentrifuging. A supercentrifuge, due to its high speed, generates a centrifugal force 13,000 times that of gravity, whereas in a centrifuge the value is seldom over 1,000 times gravity.

The small solids capacity of a supercentrifuge when used for solutions yielding more than a small amount of solid matter necessitates frequent cleaning of the bowl. A supercentrifuge could be used as an intermediate or final step in the purifying operation. With the exception of the dewaxed damar solution, it is impossible to remove all cloudiness, even by supercentrifuging. Dewaxed damar solution can be clarified by supercentrifuging, but the wax is retained in the bowl in a liquid state and cannot be compacted. When the bowl is nearly full the liquid wax is carried out with the clear effluent.

These machines can be equipped with vapor seals. The throughput is low and the operating cost is high. The rates were from 30 to 115 gal. per hour. The 115 rate was for the dewaxed damar solution which contained only about 30 per cent resin. For a 50 per cent solution, the normal throughput would be between 30 and 60 gal. per hour.

Filtering. As a final purification, it is necessary to filter the solution to remove the small amount of impurities carried through the processing. Such impurities are best removed with a plate and frame filter press or a leaf-type filter. This apparatus is not suitable for the re-

moval of dirt from the original solution, as the gelatinous matter impedes flow and greatly reduces the capacity. Once this gelatinous matter is removed by centrifuging or settling, the flow rate is tremendously increased.

As the natural resin solution to be filtered contains primarily solid fines, the use of a filter aid apparently is not needed. However, a small amount of slime will also be deposited in the frame and this may require a filter aid to increase the porosity of the cake.

Poor results were obtained on solutions containing dirt and gelatinous matter using a leaf-type filter (Table LXVII). The flow rates, even under the best conditions of pressure, temperature, and filter aid, were very low.

TABLE LXVII

Resin Solution	Temperature, °F.	Gage Pressure, lb./sq. in.	Flow Rate, gal./hr./sq. ft.
Loba dust (50% solids)	77	10–50	1.3
Loba dust (50% solids)	140	10–50	2.62
Damar (50% solids)	77	10–35	0.32
Damar (50% solids)	125	10–50	2.15
Batu (30% solids)	77	10–25	0.46
Batu (30% solids)	140	15–50	0.42

A filter should be used only on solutions that have had most of their solids roughed out by centrifuging or settling so that satisfactory flow rates can be obtained.

Solution Methods. *Natural settling.* The simplest way of removing the dirt and insoluble matter lies in solution in a solvent, followed by storage to permit settling of the foreign matter. The clean solution is decanted and the solid resin recovered by evaporation of the solvent.

This method has several drawbacks. Time is lost through the tie-up in storage. The residue contains a large percentage of solvent and resin. In order to recover this, a filtering or centrifuging operation is necessary. Certain solutions contain a cloud that settles very slowly. In order to permit complete settling, too much time is needed. Solvent loss will be appreciable. A considerable number of storage tanks will be necessary. To avoid darkening the resin solution, metal tanks must be of aluminum, nickel, stainless steel, Monel, or clad metal. The cost could be reduced if brick or concrete tanks were used and equipped with metal vapor-tight covers.

Acceleration of settling by the use of chemical compounds as addition agents. Most solutions, unless dewaxed, retain a slight degree of cloudiness even after years of settling. Although such cloudiness has no harmful effects upon the film, its removal would be desirable. Numerous attempts have been made to accelerate the clarification by chemical agents.

Metal salts, although they clarify the solution, cause excessive darkening. Water, when added to a 50 per cent manila-alcohol solution in amounts of 10 per cent, accelerates clarification without causing any precipitation of the resin. The most promising addition agent appears to be hydrogen peroxide. The resin solution obtained through such an addition was clearer and lighter. The clarification was also more rapid. Hydrogen peroxide would be ideal, for no solids would be left in the resin solution, as hydrogen peroxide decomposes to water and oxygen.

The results of such additions are given in Table LXVIII. To 90 cc. of a 50 per cent manila-alcohol solution 10 cc. of a water solution of the reagent was added. Water and hydrogen peroxide were the only reagents found that could be used for clarification without danger of darkening the resin. The storage period for settling would be markedly shortened if such additions were made.

Removal of color by clays. Decolorization by adsorptive materials such as fuller's earth and activated bauxite (impure aluminum oxide) involves passage of the solution through towers packed with the adsorbent. As the solution is fed through the tower, the coloring matter is removed from the solution. Usually the operation is carried out at slightly elevated temperatures. The degree of color removal is controlled by the time of contact, the operating temperature, the surface area, the burning temperature at which the adsorbent was prepared, and the current vitality of the adsorbent.

Solutions of damar dust were prepared in xylol and in petroleum naphtha. Glass columns, 1 in. in diameter, were used as miniature towers. These were packed with 250 cc. of adsorbent to an approximate depth of 14½ in. Three test runs at 161°F. were made on each of the two solutions. The packings were:

Packing 1 Fuller's earth burned at 900°F.

Packing 2 Bauxite burned at 800°F.

Packing 3 Bauxite burned at 1200°F.

Results are summarized in Table LXIX.

Bauxite yielded a lighter product than did fuller's earth. The colors of the treated solutions were superior to the originals. It was noticed that the originals upon standing for several days had also lightened in

TABLE LXVIII

THE EFFECT OF ADDING CLARIFYING AGENTS TO A 50 PER CENT MANILA-ALCOHOL SOLUTION

Addition Agent	30 Minutes			Overnight			10 Days		
	Deposition (cc.)	Clarity	Color	Deposition (cc.)	Clarity	Color	Deposition (cc.)	Clarity	Color
None	10	Cloudy	Brown	15	Sl. cloudy	Red-brown	14.0	Cloudy	Red-brown
H_2O	38	Sl. cloudy	Red-brown	17	Sl. cloudy	Red-brown	15.5	Clear	Red-brown
NH_4OH (28%)	28	Cloudy	Dark	17	Sl. cloudy	Dark	17.0	Clear	Dark red-brown
$AlNH_4(SO_4)_2$ (10%)	24	Sl. cloudy	Red-brown	20	Sl. cloudy	Red-brown	20.0	Nearly clear	Red-brown
NH_4VO_3 (1%)	70	Sl. cloudy	Brown	17	Sl. cloudy	Red-brown	15.0	Clear	Dark red-brown
$FeCl_3$ (10%)	30	Clear	Very dark	18	Nearly clear	Very dark	15.0	Clear	Very dark
$AlCl_3$ (10%)	41	Cloudy	Red-brown	19	Sl. cloudy	Red-brown	18.5	Clear	Red-brown
Br	55	Cloudy	Red-brown	16	Sl. cloudy	Red-brown	15.0	Clear	Red-brown
$CuSO_4$ (10%)	41	Cloudy	Brown	32	Sl. cloudy	Amber	28.0	Clear	Brown
Urea (10%)	62	Cloudy	Red-brown	16	Sl. cloudy	Red-brown	16.0	Clear	Red-brown
H_2O_2	65	Cloudy	Red-brown	18	Nearly clear	Red-brown	17.0	Very cloudy	Light red-brown
$Ca(OCl)_2$ (10%)	72	Cloudy	Red-brown	18	Cloudy	Red-brown	17.0	Sl. cloudy	Red-brown

TABLE LXIX

Packing	Damar Dust in Xylol			Damar Dust in Petroleum Naphtha		
	1	2	3	1	2	3
Rate of flow, cc. per hr.	85	90	100	75	80	90
Original resin content, per cent	23.45	23.45	23.45	18.18	18.18	18.18
Final resin content, per cent	13.05	8.41	4.80	16.37	11.32	7.70
Per cent resin loss	33.3	58.7	78.3	40.0	60.9	74.4

color, although not to the extent of the treated solutions. It was apparent that the filtering action of the packing was responsible for what had originally been believed to be solely adsorptive action. At the end of three and a half months, the only detectable differences in color between the treated and original solutions were those attributable to differences in resin content.

Because of the strong capacity of the resin itself to be adsorbed (as shown by the excessive resin losses in Table LXIX), the method does not offer much promise. Even under the best possible conditions it is likely that the resin losses would be high. For example, the decolorization of rosin from FF to WW is attended by a 25 per cent rosin loss.

Decolorization by selective solvency and precipitation methods. These methods are used in the rosin industry and show possibilities of adaptation.

A reagent such as phenol, resorcinol, furfural, furfuryl alcohol, or aniline is used as a selective solvent for the coloring matter. The rosin is cut in a cheap solvent and the reagent added at a temperature high enough to permit its miscibility with the solvent. After agitation, the mixture is cooled to a temperature at which the reagent is immiscible with the solvent, with the result that the reagent and the extracted coloring matter settle to the bottom, permitting the decantation of the supernatant light-colored rosin solution. The rosin solution is washed with water and dilute alkali solution to remove the small amount of phenol it contains. The purified rosin is recovered from the solvent by distillation. Any rosin in the reagent layer can be recovered as low-grade rosin. The reagent is also recovered.

Bleaching methods similar to the bleaching of shellac. It may be possible to decolorize natural resins by a process similar to that used in the

bleaching of shellac. The shellac is dissolved in a sodium carbonate solution, filtered, and treated with a hypochlorite solution containing 3 per cent available chlorine. When the desired lightness has been attained, the bleaching is stopped by the addition of dilute mineral acid.

Bleached shellac has the disadvantage of soon losing its solubility if care is not taken during the bleaching operation. Whether bleached natural resins would also be subject to this loss of solubility is not known. Such bleaching agents as sulfur dioxide and hydrogen peroxide should be investigated. The latter has already been mentioned for accelerating the settling of natural resin solutions. Clear manila solutions were obtained with some lightening in color.

Most of the natural resins compare favorably in color with ester gum or an average alkyd resin. Any improvement in color would increase their salability, but such additional treatment cannot add too much to the processing cost. With the efficient removal of the coloring bodies while the resin is in the dry state (as in tabling) and with the proper choice of solvents, processing would not call for a decolorizing operation.

Dewaxing of damar. Damar resin is not completely compatible with many lacquer solvents. Before being used in a nitrocellulose lacquer, the resin must be "dewaxed." This process consists in dissolving the resin in a suitable solvent and precipitating the β-resene or "wax" by adding an alcohol. The wax, after precipitation, settles rapidly, leaving a clear solution of dewaxed damar. After settling overnight, the dewaxed damar solution is decanted. Although the precipitated wax is not of a flocculent nature and normally will settle in about 3 to 4 hours, the overnight settling period is used to permit the precipitated mass to compact itself. In this manner the loss of entrapped solution is minimized and the ease of decantation increased.

A number of solvent combinations will satisfactorily dewax damar. The latitude in solvents enables the lacquer manufacturer (who generally does his own dewaxing) to select a combination that can be incorporated directly in his lacquer formula.

Solid dewaxed damar is not sold in the United States, although it has been on the market in England and continental Europe for a number of years. Dewaxed damar solutions, on the other hand, can be obtained from a number of suppliers.

Various extraction methods have been proposed and carefully investigated as well as operated on a semi-commercial scale. Difficulties minor or major in extent, of a chemical or a mechanical character, have interfered. The precipitation method remains the only one in wide use.

Both the nature of the solvent used and the grade of damar affect the character of the precipitate obtained.

For the better grades of damar, the best results are obtained by following the widely used procedure of dissolving the resin in an equal weight of toluol and adding an equal weight of alcohol. For the poorer grades, however, the toluol is better replaced by a mixture of ⅔ light petroleum naphtha and ⅓ ethyl acetate, or by ethyl acetate 12.5 per cent, acetone 12.5 per cent, and benzene 75 per cent. By increasing the proportion of damar to as much as 2.5 parts, the toluol procedure may be made to give good results with all grades of damar. The wax-free solution is of low viscosity, about 0.5 poise (A on the Gardner-Holdt scale) and because of its low solvent content—about 45 per cent—is adaptable to a wider variety of lacquer formulations.

The actual β-resene content of damar resin varies from 8 to 11 per cent. Generally, in dewaxing damar there is a total loss of 15 to 20 per cent, as some of the solution is occluded in the precipitate. The dewaxed damar is soluble, or mostly soluble, in nearly all the common organic solvents.

A desirable method of dewaxing damar would involve an extraction of percolation procedure. Dewaxing experiments have been made using varying proportions of resin, aromatic solvent, and alcohol (Table LXX). The damar was dissolved in the coal-tar solvent and the alcohol added with stirring. These proportions of solvents form constant boiling mixtures in each case.

TABLE LXX

No.	Batavia Damar (*Grams*)	Aromatic Solvent (*Grams*)	Alcohol (*Grams*)
1	20	20 benzol	13.5 methyl alcohol
2	20	20 benzol	9.5 ethyl alcohol
3	20	20 benzol	11.5 isopropyl alcohol
4	20	20 toluol	46.5 ethyl alcohol
5	20	20 toluol	45. isopropyl alcohol

Numbers 4 and 5 gave the best separation of wax from wax-free resin.

Samples of crushed damar were extracted in a Soxhlet extractor using a constant boiling mixture of 46 cc. toluol and 112 cc. isopropyl alcohol. In one run the resin was placed in a paper Soxhlet thimble. In others,

the resin was wrapped in small pieces of cheesecloth, each package containing 10 to 15 grams of resin, and 3 to 4 such miniature sacks were placed in the upper chamber of the extractor. A satisfactorily effective separation of wax from wax-free resin was obtained in each method.

It was desired to investigate the possibility of an extraction process of dewaxing to be used on the resin as received. A 2-liter flask was fitted with a vapor outlet tube leading to a reflux condenser which emptied into a can from the bottom of which a siphon led back to the flask—in principle a large-scale Soxhlet extractor. One hundred grams each of damar B, C, D, and A/D were wrapped in separate cheesecloth packages and placed in the can. Four hundred sixty-three cc. of toluol and 1,088 cc. of alcohol (a constant boiling mixture) were placed in the flask and boiled. When about 800 cc. of solvent had boiled over, the siphon emptied the liquid contents of the can into the flask. When this had occurred six times, the operation was stopped and the resin examined. The β-resene which had been separated in the outer layers of the packages was very pure, as indicated by its melting point of 203°C. However, there was considerable unattacked resin. Table LXXI shows the percentages of the original resin samples remaining in each package.

TABLE LXXI

Sample	Residue (*Per cent*)	Wax in Residue (*Per cent*)	Wax-Free Resin in Residue (*Per cent*)
B	34.7	10.6	24.1
C	47.3	12.5	34.8
D	44.7	12.4	32.3
A/D	39.4	10.4	29.0

An extraction process is a possibility if agitation of some sort could be used, or if the resin could be extracted in a ground condition. In the latter method, mechanical difficulties are met, as the ground resin softens and clogs up the pores of the resin chamber. The clogging can be moderated by mixing inert material of varying sizes with the resin. Such an extraction process is satisfactory if enough inert material is present. In such a dewaxing process, the wax can be recovered by extracting the residue with a wax solvent. Unless most of the woody material is first removed, any extraction operation will cause a darkening

of the solution due to the leaching action of the solvent. If the extraction is hot, the darkening will be more severe than if carried out cold.

Batu, pale east india, and black east india can be dewaxed and used in lacquers. The wax contents of these three resins are considerably higher than that of damar, being approximately 50 per cent. The dewaxed solutions of such resins are not so light as a dewaxed damar solution. Insufficient work has been done on the properties of these dewaxed resins and their waxes, but it is believed that the waxes are similar to damar wax. Batu and black east india would represent cheap sources of damar wax should the demand exceed the amount obtained as a by-product of dewaxing.

It is possible that the resin remaining in tabling residues could be recovered by a similar extraction process, although a straight solution recovery is cheaper.

Drying. Regardless of what processing method is used, the final cleaned resin will be in solution form and the problem of evaporating the solvent to secure the solid resin presents itself.

Inasmuch as natural resins are organic bodies, they are sensitive to heat and darken when exposed to elevated temperatures. Drying should be done either under a vacuum or very rapidly. In order to secure thorough drying, at least below 3 to 4 per cent residual solvent content, it is preferable to dry in a thin sheet or in the form of pellets. This indicates the use of a drum or spray dryer. Because of their relatively poor heat economy, spray dryers are not usually recommended. Of the two, a drum dryer appears to be the more suitable.

In its simplest form a drum dryer consists of a hollow metal drum or cylinder equipped with trunnions to permit rotation about its longitudinal axis. Steam is fed into this hollow drum through one of the trunnions. The drum is partly immersed in a tank filled with the solution to be evaporated and dried. As the drum rotates, it picks up a film of solution. Owing to the heat of the drum the solvent is driven out of the film. After more than two-thirds of a revolution, the film consists entirely of resin which can be taken off by a scraper knife. To accelerate the evaporation of solvent, a hood can be placed over the tank and drum, completely enclosing it, and a vacuum applied.

Because of excessive foaming, it is not possible to use such a dip feed for natural resin solutions. An overhead drip feed is used instead. This type of dryer is equipped with double drums.

The capacity of such dryers is governed by the surface area of the drum, the speed of rotation, the steam pressure, the solvent's latent

heat of vaporization, and the thickness of the film. For a given feed viscosity, a thick film of solution not only contains more solvent than a thin film, but its rate of drying is reduced because of the greater resistance to flow of heat and vapor through it. Greater capacity is obtained by drying thin films at a fairly high rate of rotation. With very thin films and high roll speeds, the time of contact of the material with the hot roll is greatly reduced.

Heat loss from a drum dryer is low. From the tests that have been run, it is estimated that 3 to 7 lb. of solvent can be evaporated per hour per square foot.

Drum drying of solutions of damar, dewaxed damar, dewaxed batu, and manila DBB was attempted by the authors usually with satisfactory results. Solutions of damar in Solvent Naphtha No. 4,[1] manila DBB in denatured alcohol, dewaxed batu in 2 toluol to 1 Solvent Naphtha No. 4, and dewaxed damar in 2 parts Solvent Naphtha No. 4 to 1 denatured alcohol, were tested. The samples of manila DBB and dewaxed batu, both dried under vacuum, and the dewaxed damar, dried under atmospheric pressure, were loose flakes with no cohesion between flakes. The manila DBB and dewaxed batu when dried under atmospheric pressure were also of a flaky nature, but because of their relatively high residual solvent content there was a tendency toward blocking. The blocking was very loose and easily broken up. The damar sample was a solid mass of resin.

The manila DBB and the dewaxed batu solutions could be dried satisfactorily on the vacuum drum dryer. The damar and dewaxed damar solutions, owing to the low softening points of the resin, would not solidify, and were removed by the scraper knives in a thick liquid, semi-solid, or soft plastic state. This condition existed regardless of temperature and speed. The heating medium was varied from a subatmospheric pressure of 20 in. of mercury (4.6 lb. per sq. in. absolute pressure) to 60 lb. per sq. in. gage (75 lb. per sq. in. absolute). At higher temperatures the tendency toward fluidity increased.

Attempts were then made to dry the solutions on an atmospheric two-stage dryer by drying on the upper drums and cooling on the lower. Although the residual solvent contents of these products are high, particularly for the dewaxed batu, they can be reduced by increasing the steam pressure or by lowering the roll speed. Results of both methods are given in Table LXXII.

[1] Solvent Naphtha No. 4 is a straight paraffin petroleum solvent with a boiling range of 77 to 121°C. and a specific gravity of 0.72.

TABLE LXXII

DRUM DRYING OF NATURAL RESIN SOLUTIONS

Resin Solution		Dewaxed Batu					Manila DBB	Damar	Dewax. Damar	Manila DBB	Dewax. Batu
Drying apparatus		Double-drum vacuum dryer, stainless steel drums (6 in. × 8 in.)						Two-stage atmospheric dryer, cast-iron drums			
Test Number*		1	2	3	4	5	6	7	8	9	10
Barometer reading	in. of Hg	29.45	29.45	29.45	30.05	30.05	29.44	..	..	..	..
Solids in original solution	%	24.93	24.93	24.93	24.93	24.93	30.83	47.49	30.40	30.83	24.93
Steam press. in drums—start	lb./sq. in.	8	8	14	13	9.5	7.1	..	..	..	..
Steam press. in drums—finish	lb./sq. in.	8	8	14	13	9.5	7.1	..	..	..	..
Drum speed	r.p.m.	5.125	6	10	10.25	11.25	4.75	..	..	..	..
Vacuum—start	in. of Hg	?	?	?	?	?	27.70	None	None	None	None
Vacuum—finish	in. of Hg	?	?	?	?	?	27.70	None	None	None	None
Steam press. (upper drums)	lb./sq. in.	..	..	..	..	..	..	16	10	16	22.25
Drum speed (upper drums)	r.p.m.	..	..	..	..	..	..	1.0	1.0	1.0	1.875
Temp. of cooling H_2O (lower drums)	°F.	..	..	..	..	..	..	49	49	49	49
Drum speed (lower drums)	r.p.m.	..	..	..	..	..	..	2.75	2.75	2.75	2.75
Duration of test	min.	30	20	5	10	6	53.5	18	16	18.5	16
Weight of dry material	lb.	0.72	0.65	0.18	0.48	0.36	1.87	1.16	0.84	1.34	0.97
Capacity of dry material	lb./hr.	1.44	1.95	2.16	2.88	3.60	2.10	3.86	3.15	4.34	3.63
Drying rate	lb. / hr./sq. ft.	0.72	0.975	1.08	1.44	1.80	1.05	1.93	1.57	2.17	1.81
"Moisture" in dry material	%	2.99	2.76	3.16	2.85	2.89	2.15	6.42	2.28	4.12	12.50

* *Tests 9 and 10 came off the drum in thin, plastic sheets.*

TABLE LXXIII

COLORS OF 50 PER CENT SOLUTIONS

Resin	Color
Damar from atmospheric two-stage dryer (in toluol)	6–7
Dewaxed damar atmospheric two-stage dryer (in toluol)	7–8
Dewaxed batu atmospheric two-stage dryer (in toluol)	12
Manila DBB atmospheric two-stage dryer (in alcohol)	6–7
Manila DBB from vacuum drum dryer (in alcohol)	6–7
Dewaxed batu from vacuum drum dryer (in alcohol)	12

The solid samples obtained were dissolved in either toluol or alcohol and colors taken (Table LXXIII).

Because of the short time of contact, resins dried on the atmospheric dryer were no darker in color than those dried on the vacuum dryer, although the former had cast-iron drums whereas those of the latter were of stainless steel. In neither did the drying operation cause any darkening in color.

The quick-cutting property of these flake samples is an advantage to the consumer, for it is possible to prepare 50 per cent solutions in about 10 minutes or less merely by shaking.

The resins dried under atmospheric conditions had higher residual solvent contents than those dried under vacuum, and were prone to flake or block together. The latter resins after drying were individual flakes with no cohesion between them. The critical solvent content appears to be in the neighborhood of 3.5 per cent. Above this, blocking is likely and below it the possibility is negligible.

Model Resin Purification Plant. To illustrate the various operations involved in resin purification, flow sheets have been prepared for a model resin purification plant. The layouts are, of course, tentative and subject to the modifications that a pilot plant and economy would dictate.

The final choice of solvents will depend upon both economic and operating factors. In the flow sheets, therefore, the solvents used are purely nominal, with hydrocarbon solvents being specified for damar type resins and alcohol for the manilas. The flow sheets are given in Figs. 51, 52, and 53 (Flow Sheets I, II, and III). Flow sheet I will handle all types of damar resin, i.e., black and pale east indias and batu. Flow sheet II covers all the manila resins—pontianaks, lobas, melengkets, CBB, and DBB.

The grades of purified resin have not been specified. For the manilas it may be well to market in three grades: soft (melengkets), half-hard (lobas), and hard (pontianaks, CBB, and DBB). Boea, if processed,

would also be in this last group. If the color of certain grades cannot be improved, two or more color gradings will be necessary within each of the groups; this applies to both manilas and damars.

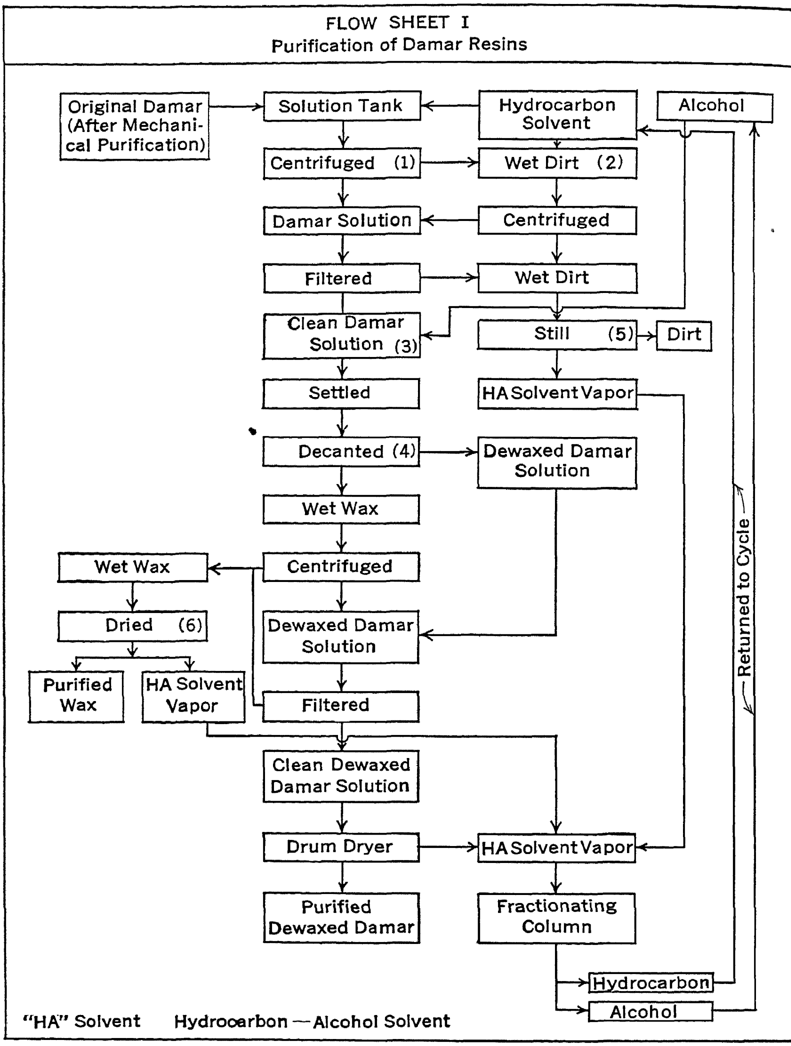


FIG. 51.

In both flow sheets no mention is made of such preliminary treatment as tabling, flotation, or grinding. The necessity for such treatment will

be determined by the grade and condition of the original resin. Furthermore, all operations given in these flow sheets are entirely of a mechanical nature and do not include such chemical methods as decolorization or the use of addition agents.

Flow Sheet I. (Fig. 51.) The damar resin is dissolved in hydrocarbon solvent and passed to the centrifuge (1) where most of the insoluble matter is roughed out. This wet dirt (2) can be washed with solvent to extract the resin it contains, after which the mass is centrifuged and the solution fed back to the main body. Washing should be done only if the resin content warrants it. Because some fine impurities will always be carried over from the centrifuging operation, it is necessary to filter the solution at this point. Either a plate and frame or leaf-type filter can be used.

At (3) a clear damar solution is on hand to be dried or to be dewaxed. For dewaxing, alcohol is added to precipitate the wax. The solution could be centrifuged immediately or permitted to settle. Inasmuch as the wax settles rapidly, it would be preferable to settle and decant (4) the clear dewaxed solution, leaving just enough solution in the tank to permit the wax to be easily transferred to a centrifuge. The wax is centrifuged to remove the dewaxed damar solution which is then mixed with the decanted solution, filtered if necessary to remove any particles of wax, and dried on a drum dryer.

The solvent vapor issuing from the dryer will contain both alcohol and hydrocarbon solvent. In order to separate the two components it will be necessary to pass the vapor through a fractionating column.

The wet dirt obtained from the various filtering and centrifuging operations is distilled (5) to recover the solvent present.

The wax as it comes from the centrifuge will contain some resin solution. If no further purification is done, the dried wax will contain a small percentage (perhaps up to 5 per cent) of damar. The damar could be removed by dissolving the wax in hydrocarbon solvent and reprecipitating with alcohol, but this procedure would have to be repeated several times before all the damar was removed. In the flow sheet, as given, the wax undergoes no further treatment after centrifuging other than drying (6). The wax cannot be dried on a drum dryer, since it is a plastic mass rather than a solution as it comes from the centrifuge. The solvent it does contain can be driven off by heating in a steam pan, using either atmospheric or vacuum pressure. This, however, will result in some darkening of the wax. As an alternative, a drum dryer can be used if the wax is first dissolved in a hydrocarbon solvent after centrifuging.

Flow Sheet II. (Fig. 52.) The steps involved in manila purification are duplicates of the damar treatment, save that no dewaxing is necessary.

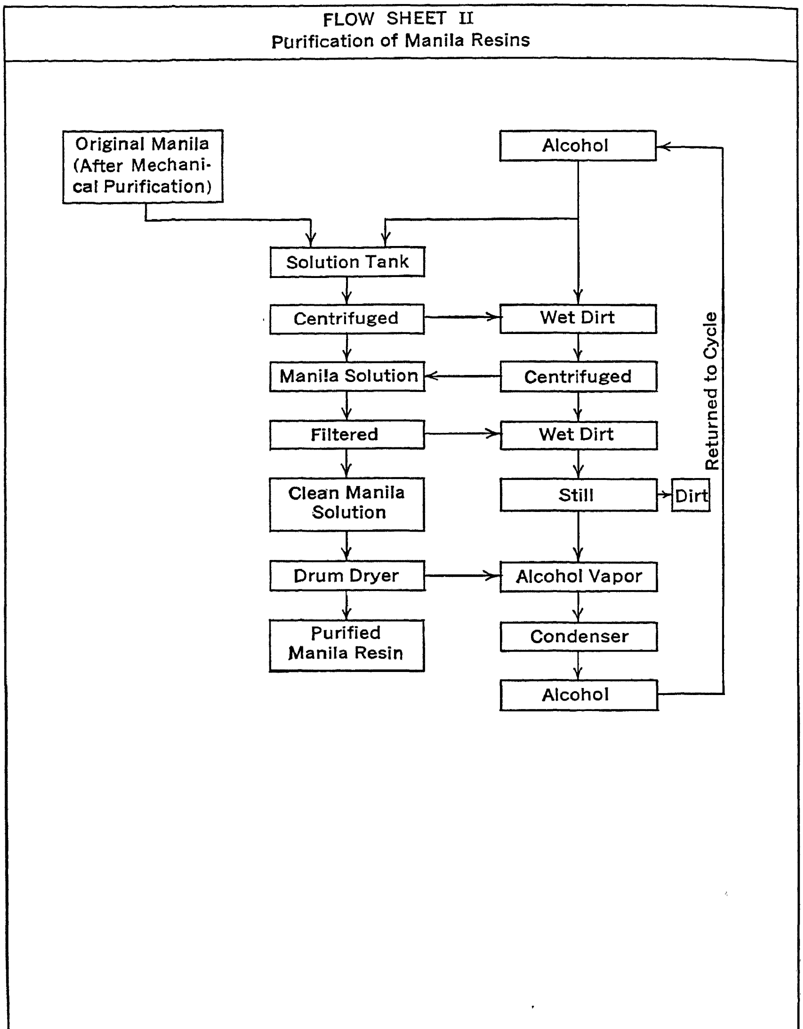


FIG. 52.

Flow Sheet III. (Fig. 53.) From the dewaxing operation in flow sheet I, a combination solvent (hydrocarbon and alcohol) is obtained. To

separate these two would necessitate the use of a fractionating column of considerable height. The cost of such a unit would be disproportion-

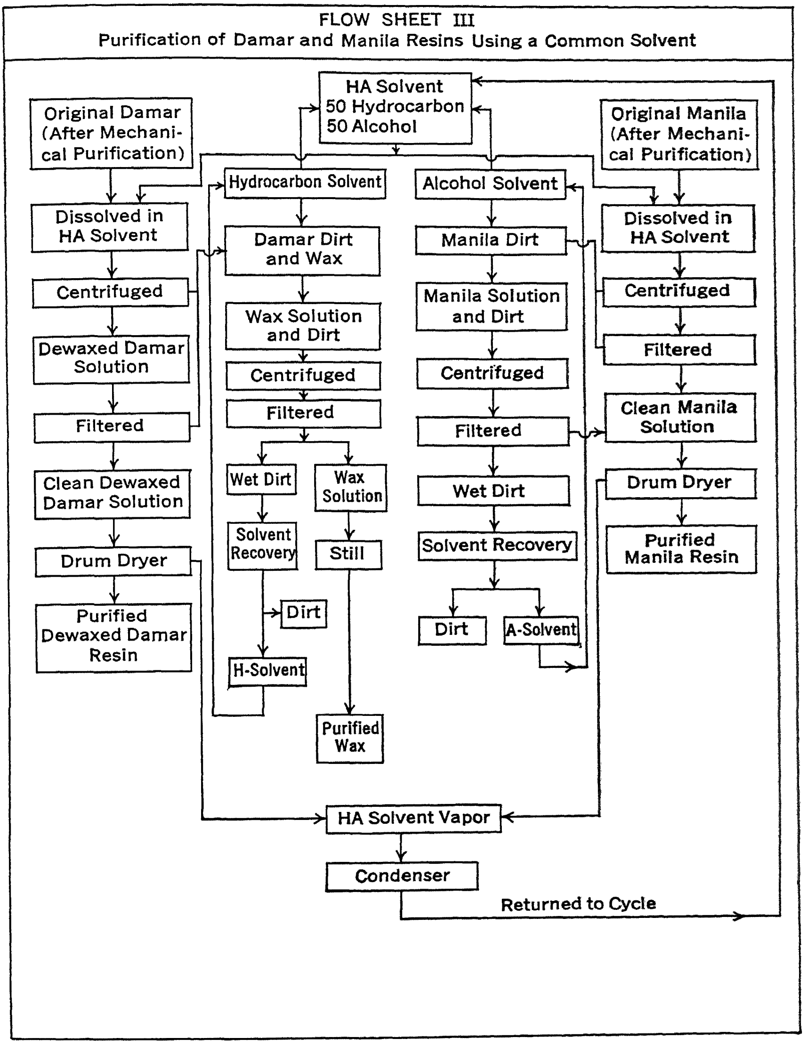


FIG. 53.

ately high in a plant of this type. If, instead of using only hydrocarbon as the original solvent, a hydrocarbon-alcohol solvent be used, the existing HA solvent vapor could be condensed and returned to the cycle

ready to dissolve a fresh lot of resin, with the need for an expensive column eliminated.

The damars are soluble in such a combination; the only difference in the operation of the process would be that the dirt and wax would be taken out together rather than separately. The separation of wax from dirt would involve solution in straight hydrocarbon solvents in a later step.

Combination hydrocarbon-alcohol solvents also dissolve Manila resins if some aromatic hydrocarbon be present. Thus, one solvent could be used for both damars and manilas, with additions of hydrocarbon or alcohol being made whenever necessary to adjust its solubility to the particular resin on hand.

The use of a combination solvent could be confined to the damar resins, but the solvent cost for the manila purification process would be reduced if part of the alcohol were replaced with a cheap petroleum solvent.

Flow sheet III, outlining the operations involved in the purification of damar and manila resins by the use of a common solvent, is a direct combination of flow sheets I and II with but slight modification. Such a plant would be very flexible and capable of handling any type of resin.

Although a specific piece of equipment may be mentioned several times in these flow sheets throughout the entire chain of processing operations, it is obviously the same unit being used repeatedly.

CHAPTER XVIII

OIL VARNISHES

During the nineteenth century, progress in varnish making consisted largely of finding new and more favorable combinations of materials already known and in small variations in the methods of cooking them together. The varnishes were made from linseed oil, natural resins, rosin, lime, lead and manganese, and turpentine. They were slow drying and of moderate durability.

Varnish manufacture was a secret art and all information pertaining to it and its raw materials was jealously guarded. Up to recent years the literature on natural resins has always been meager despite the tremendous quantities used. Published accounts of current methods of varnish making have been practically non-existent.

In the second decade of the twentieth century, China wood oil and ester gum were coming into wide use. In 1912 the New York Produce Commission established an official method of testing. Ester gum found favor because of its ready solubility and neutral character. China wood oil presented new problems and many were the exasperating experiences with the tricky stuff. These products and the synthetic resins which came into the market soon after were becoming important at the time when manufacturing was expanding into the modern phase of large-scale production. The variety of products manufactured created a correspondingly great demand for an almost infinite variety of coating materials for their decoration and preservation. An integral part of all this was the greatly increased dependence of industry on the inventions and guidance of the chemist.

The synthetic resins were new products and a market had to be built up for them. They were invented by chemists, and scientific methods were used in determining their varnish-making values and in applying them. A result was the technical salesman who knew what his product could do. He was backed up by a laboratory which was willing to aid the customer in adapting these new products.

In contrast, the natural resins had been known since varnish making first began. They had always had their market and their users knew more about their varnish-making properties than did the merchants who sold them. Very few of these merchants had technical staffs or

were in a position to aid the varnish maker in adapting the natural resins to meet the many new demands made upon them by the great increase in industrial activity.

Realization of the need for a critical study of the values of natural resin as compared with synthetic resins, as well as a desire to present to consumers the benefits of a scientific study of the properties and uses of natural resins, prompted importers and exporters to join hands in the financing of such work. One phase of the research program subsequently carried out produced valuable information on natural resin varnishes.[1]

At the time synthetic resins were being developed and put on the market, China wood oil was still a new product whose good properties were as yet imperfectly realized. Varnishes containing China wood oil naturally were studied by the chemist engaged in devising formulae. Varnishes of outstanding properties were produced by the combination of synthetic resins with this oil. These were seized upon by the synthetic resin manufacturer who widely publicized them throughout the varnish field. Without realizing it, the manufacturer of synthetic resins was responsible for spreading the belief that the excellent properties of synthetic resin varnishes were due chiefly to the resin used. It is remarkable how great a proportion of synthetic resin formulae include a large amount of China wood oil.

Meanwhile, natural resin varnish formulation continued along its former line. Linseed oil always had been the chief varnish oil, and so far as natural resins were concerned, it continued to be. A condition eventually was born in which it became the usual thing to think of synthetic resins in terms of China wood oil, and natural resins in terms of linseed oil. When a natural resin varnish was compared in performance or properties with a synthetic resin varnish, a comparison also was being made (unwittingly) of a China wood oil film with a linseed oil film. Under such circumstances, the naturals proved inferior to the

[1] C. H. Allen, "Recent Developments in Natural Varnishes," *Drugs, Oils & Paints,* October, 1934.

C. H. Allen and K. M. Sprinkel, "Recent Developments in Natural Resin Varnish—II," *Official Digest,* Fed. Paint and Varnish Prod. Clubs, February, 1935.

C. H. Allen and K. M. Sprinkel, "Recent Developments in Natural Resin Varnish—III," *Official Digest,* Fed. Paint and Varnish Prod. Clubs, March, 1935.

C. L. Mantell and K. M. Sprinkel, "Natural Resins for the Varnish Industry," *Ind. Eng. Chem.,* 27, 1369-73 (1935).

C. L. Mantell, C. H. Allen, and K. M. Sprinkel, "Research on Natural Resins and Their Varnishes," *Official Digest,* Fed. Paint and Varnish Prod. Clubs, January, 1936.

synthetics. Were the conditions reversed, i.e., synthetic-linseed oil varnishes compared with natural-China wood oil varnishes, the results might be just as sharply in favor of the naturals. Furthermore, although the naturals give satisfactory films using linseed oil, the same cannot be said about a number of the synthetics. Deprive some synthetic resin varnishes of their China wood oil content, and they are inferior to natural resin-linseed oil varnishes.

Many properties attributed to synthetic resin varnishes are due to properties inherent in China wood oil and not to the resin. Certainly, when quick-drying enamels and varnishes became prominent they were generally credited to synthetic resins, whereas it is now known that natural resins with China wood oil also give quick-drying varnishes and enamels.

The work of Mantell, Allen, and Sprinkel[2] has clearly demonstrated that natural resin varnishes can be made using China wood oil which are equal or superior to those containing modified-phenolic resins. This parity or excellence has been confirmed by both laboratory and weathering tests.

Several hundred varnishes were prepared and their properties determined by numerous laboratory tests and by weathering. Care was taken to formulate and cook them under conditions as nearly identical as were practicable. The natural resins were run in the customary way and then the China wood oil, heated to 400°F., was added and the varnish cooked at 560°F. until the desired body was reached. The bodied linseed was then added as a check oil and the batch thinned.

Each synthetic resin varnish was cooked by the methods recommended by their manufacturers, then checked and thinned. Many of these cooks—except for running the resin—were the same as those described for the natural resins. These varnishes are identical except for the resin used, and therefore make possible comparisons of the relative values and properties of each resin in varnishes of this type of formula.

After aging for a week or more, the varnishes were centrifuged and soluble-type driers were added. The ratio of metals used was chosen to give a balanced drier capable of a wide variety of uses. The ratio of lead to cobalt was about 45 to 1, to give through drying with a minimum of top drying and risk of destructive action. The quantity used was kept low, being 0.4 per cent lead, 0.03 per cent manganese, and 0.0088 per cent cobalt calculated as metals and based on the weight of drying oil.

[2] *Loc. cit.*

Eight "all-purpose" floor and spar-type varnishes, purchased at paint and hardware stores, were "controls."

Fifteen-, 25-, and 50-gallon varnishes were made. Separate groups of varnishes were made in which the oils were 75 per cent, 90 per cent, or 100 per cent China wood oil and the remainder bodied linseed. The "gallonage" of a varnish is the number of gallons of oil in which 100 lb. of resin are incorporated.

The formulation for each group of varnishes was identical except as to the resin used. A typical 25-gallon formula is as follows:

Formula 1

100 lb.	hard dark amber congo (No. 11)
21.5 gal.	(170 lb.) China wood oil
3.5 gal.	(30 lb.) 4-hr. linseed oil
36.9 gal.	(240 lb.) varnolene
8.4 gal.	(60 lb.) high-flash naphtha

All varnishes contained 50 per cent non-volatile. The higher solvency thinners were used in all the varnishes because some of the phenolic resins required them. All exposures were at a 45-degree angle (south) in Cincinnati.

Data showing the physical properties of 50-, 25-, and 15-gallon varnishes made from single natural and synthetic resins appear in Tables LXXIV, LXXV, and LXXVI.

The kauri numbers of these 50-gallen varnishes naturally were high. The average kauri number for three modified synthetics was 143; that for the cheaper natural was 145. The gloss of the naturals was about the same as for the synthetics. (These varnishes were not formulated for gloss. In special formulations it is known that the naturals give better gloss than the synthetics.) The natural resin varnishes dried just as fast as those from synthetic resins. China wood oil is the primary cause of rapid drying. The drier content of these varnishes was low. Four of the six natural resin varnishes and two of the modified synthetics were gas-proof. The natural resin varnishes gas-proof as well as the modified synthetics do. The hardness of the naturals was the same as that of the modified synthetics. The natural resin varnishes withstood the action of boiling water for one hour perfectly, as did the synthetics also. After four days in cold water, each of the varnishes listed (except one commercial spar) suffered a moderate loss of gloss. The natural resin varnishes passed the test as well as any of the synthetics.

One hour in boiling 5 per cent Ivory soap, as would be expected, softened nearly all these 50-gallon varnishes. The ones from bold black

TABLE LXXIV

PHYSICAL PROPERTIES OF SINGLE RESIN 50-GALLON VARNISHES

Formula No.	Resins	Per Cent China Wood Oil	Kauri Number	Relative Gloss	Gas-Proofness	Hours till Tack Free	Viscosity	Relative Hardness after 7 Days	Loss of Gloss or Softening after		
									1 hr. boiling water	1 hr. in 5% Ivory soap	4 days in water
2	No. 1 brown kauri	90	150	3	OK	2	B	4	OK	Mo	Mo
3	Genuine bold pontianak	90	150	6	F	2	C	4	OK	VM	Mo
4	Bold black east india scraped	90	150	3	OK	$2\frac{1}{2}$	C	3	OK	OK	Mo
5	Pale bold east india	90	130	4	OK	$2\frac{1}{2}$	E	5	OK	VM	Mo
6	Manila DBB chips	75	160	3	OK	2	D	2	OK	VM	Mo
7	Boea medium dark	75	150	4	F	2	G	4	OK	M	Mo
8	Batu bold scraped	90	130	5	OK	4	D	4	OK	Mo	Mo
9	Concentrated phenolic No. 1	100	200	2	OK	2	H	5	OK	Mo	Mo
10	Modified phenolic No. 4	90	150	6	OK	3	B	4	OK	M	Mo
11	Modified phenolic No. 5	90	150	4	F	2	C	3	OK	M	Mo
12	Modified phenolic No. 6	90	130	7	OK	$2\frac{1}{2}$	B	4	OK	VM	Mo
	Commercial spar No. 1	..	110	6	F	5	G	2	OK	VM	OK
	Commercial spar No. 2	..	60	4	OK	5	D	3	OK	VM	Mo
	Commercial spar No. 5	..	150	9	OK	5	F	3	VM	M	Mo
	Commercial spar No. 7	..	70	9	OK	5	E	3	OK	VM	Mo

F failed; VM very much softening; M much softening; Mo moderate softening.

TABLE LXXV

PHYSICAL PROPERTIES OF SINGLE RESIN 25-GALLON VARNISHES

Formula No.	Resins	Per Cent China Wood Oil	Kauri Number	Relative Gloss	Gas-Proofness	Hours till Tack Free	Viscosity	Relative Hardness after 7 Days	Loss of Gloss or Softening after: 1 hr. boiling water	1 hr. in 5% Ivory soap	4 days in water
13	No. 1 brown kauri	90	100	7	F	2	C	4	OK	M	Mo
14	No. 1 brown kauri	75	100	7	F	2½	B	4	OK	M	Mo
15	Bold pontianak	90	100	6	F	2	C	4	OK	M	Mo
16	Bold pontianak	75	100	8	F	2	D	3	OK	Mo	Mo
17	Hard dark amber congo	90	110	4	F	2	F	4	OK	M	Mo
18	Hard dark amber congo	75	100	4	F	2	E	4	OK	Mo	Mo
19	Hard light amber congo	90	90	7	F	2	C	4	OK	M	Mo
20	Clean ivory congo	75	90	5	F	2	E	3	OK	M	Mo
21	Bold black east india scraped	90	70	6	OK	2	F	3	OK	Mo	Mo
22	Bold black east india scraped	75	60	7	F	2½	C	3	OK	M	Mo
23	Batu bold scraped	90	70	7	F	2½	D	3	OK	Mo	Mo
24	Batu bold scraped	75	70	8	F	2½	C	3	OK	Mo	Mo
25	Pale bold east india	90	50	7	F	2½	H	4	OK	M	Mo
26	Pale bold east india	100	80	6	F	3	G	3	OK	Mo	Mo
27	Manila DBB chips	75	80	7	F	2½	C	3	OK	Mo	Mo
28	Boea medium dark	75	110	5	OK	2	B	4	OK	Mo	Mo
29	Concentrated phenolic No. 1	90	110	5	OK	3	E	3	OK	OK	OK
30	Modified phenolic No. 7	90	70	6	F	2½	B	3	VM	M	OK
31	Modified phenolic No. 5	90	70	6	F	3	C	3	OK	Mo	OK
32	Modified phenolic No. 8	90	50	8	F	3½	C	4	OK	OK	OK
	Commercial spar No. 2	. .	60	4	OK	5	D	3	OK	VM	Mo
	Commercial floor No. 4	. .	60	5	OK	5	E	4	OK	M	Mo
	Commercial all-purpose No. 7	. .	70	9	OK	5	E	3	OK	VM	Mo

F failed; VM very much softening; M much softening; Mo moderate softening.

scraped and kauri were outstanding in their resistance and were superior to any of the modified phenolics. The other naturals averaged as high as the modified phenolics.

The data reveals that in all this series of tests on 50-gallon varnishes the natural resins equaled or exceeded the values of modified phenolics.

The kauri numbers of the 25-gallon natural resin varnishes averaged much higher than those for the modified synthetics. The boea medium dark and hard dark amber congo varnishes had kauri numbers as high as that of the varnish from the concentrated phenolic resin and were more than double that of the varnish from the poorest modified-phenolic resin. Ten of the sixteen natural resin varnishes had kauri numbers much higher than that of the best modified phenolic, only two of the poorest were as low as modified phenolic No. 8. The weather resistance shown by these panels was equally as favorable to the natural resins.

The average gloss number of the sixteen natural resin varnishes was about 10 per cent higher than that for all the phenolics.

Two natural resin varnishes were gas-proof, whereas none of the varnishes from modified phenolics was gas-proof. The drying rate of the natural resin varnishes exceeded that of the modified phenolics. The hardness of the naturals was greater than that of all the phenolics.

All the varnishes passed the test of 1 hour in boiling water except one modified phenolic which completely failed. All but two varnishes were considerably softened by 1 hour in boiling soap solution. One concentrated and one modified phenolic varnish passed the test. The remainder of the phenolic varnishes and all the natural resin varnishes were equally divided between moderate and much softening.

The natural resin varnishes suffered moderate loss of gloss but no rusting of the metal panels after four days in cold water, whereas the phenolics retained their gloss. In view of the superior weather resistance for the 25-gallon natural resin varnishes, this result was unexpected.

The purchased varnishes of a type similar to these 25-gallon varnishes showed low kauri numbers, greater gloss and gas-proofness, slower drying, and low resistance to boiling soap solution.

These tests of the 25-gallon varnishes again demonstrated the superior qualities of the natural resins: much higher kauri numbers than the modified phenolics, supported by weathering tests; resistance to soap and cold water equal, or nearly equal, to the modified phenolics; greater gloss and hardness; more rapid drying; and every natural resin varnish passed the boiling water test, whereas one of three modified synthetics failed.

TABLE LXXVI

PHYSICAL PROPERTIES OF SINGLE RESIN 15-GALLON VARNISHES

Formula No.	Resin	Per Cent China Wood Oil	Kauri Number	Relative Gloss	Gas-Proofness	Hours till Tack Free	Viscosity	Relative Hardness after 7 Days	Loss of Gloss or Softening after		
									1 hr. boiling water	1 hr. in 5% Ivory soap	4 days in water
33	No. 1 brown kauri	90	30	7	F	3	C	5	OK	Mo	Mo
34	Bold pontianak	90	30	7	F	$2\frac{1}{2}$	B	5	OK	VM	OK
35	Hard dark amber congo	90	20	6	F	2	C	4	Mo	OK	Mo
36	Bold black east india scraped	90	0	6	F	3	D	5	OK	VM	Mo
37	Batu bold scraped	90	0	7	F	3	C	5	OK	VM	Mo
38	Pale bold east india	90	0	5	OK	$2\frac{1}{2}$	E	3	Mo	Mo	Mo
39	Modified phenolic No. 7	90	10	6	F	$2\frac{1}{2}$	B	4	OK	Mo	Mo
	Commercial 4-hr. floor No. 3	. .	0	6	OK	5	E	4	OK	VM	Mo
	Commercial quick-drying No. 6	. .	0	9	OK	5	F	4	OK	VM	Mo
	Commercial floor No. 8	. .	20	9	OK	5	D	4	OK	VM	OK

F failed; VM very much softening; Mo moderate softening.

There were only a few varnishes in the 15-gallon group. The results of the laboratory tests on them were similar to those for the 25- and 50-gallon varnishes. The kauri numbers of the harder natural resin varnishes were 30, 30, and 20, as compared with 10 for the modified-phenolic resin varnish. Even in these short oil varnishes where the ratio of China wood oil to resin is low, the average drying rate of the natural resins equaled that of the modified phenolic. The gloss and hardness of the natural resin varnishes were superior and their resistance to hot and cold water and boiling soap solution averaged about the same as that of the synthetic resin varnish.

It has been shown that, when compared with modified-phenolic resins in high China wood oil content varnishes, natural resins yield superior gloss and hardness and dry at least as rapidly as the modified phenolics do. Their resistance to hot and cold water and to boiling soap solution is excellent.

This demonstration of these qualities for natural resin varnishes containing high percentages of China wood oil strongly supports the claim that many values which have been widely credited to synthetic resins are actually due to China wood oil.

Weathering tests of single resin natural and synthetic varnishes show that the naturals possess a marked advantage in the manner of their weathering. As all coatings eventually fail and require revarnishing, the condition of the weathered surface is a primary factor in the expense of refinishing. Varnish films which fail by severe checking and cracking present a rough surface with much of the wood exposed and other portions covered with poorly adhering masses. Such a finish requires considerable surface treatment before it is suitable for revarnishing. On the other hand, failure by fine checking does not seriously impair the integrity of the film. Little or no wood is exposed and a minimum of surface preparation is needed. An examination of photomicrographs used as illustrations in the original articles[3] will reveal that the weathered films of natural resin varnishes were in much better condition for revarnishing than those from modified-phenolic varnishes. After six months of weathering, the photomicrograph of a 25-gallon pale east india varnish, No. 26, showed the redwood panel to have suffered but superficial damage. The film was intact and still able to give complete protection to the panel. The satisfactory character of its weathering was demonstrated by its fine, shallow checking

[3] C. H. Allen and K. M. Sprinkel, *Official Digest,* Fed. Paint and Varnish Prod. Clubs, March, 1935; C. L. Mantell, C. H. Allen, and K. M. Sprinkel, *ibid.,* January, 1936.

and the absence of deep cracks which would expose the wood. Varnishes containing pontianak, batu, and congo, respectively, yielded similar results.

The best of all the 25-gallon varnishes tested proved to be one prepared from a boea resin. Checking was almost completely absent and the wood grain could be observed quite clearly through the varnish film. It was only slightly inferior to most of the 50-gallon synthetic resin varnishes and definitely superior to two of them.

Three 25-gallon varnishes containing different modified-phenolic resins were weathered for the same length of time and at the same location as the above 25-gallon natural resin varnishes. In formulation, cooking methods, and all other manipulation, these resins were given treatment as favorable to their requirements as that accorded the naturals. The decidedly poor weather resistance of these modified-phenolic varnishes was shown by the large areas of exposed wood. The blistered and deeply checked condition of the remainder of the films revealed the extent to which the elements had been able to attack the varnish from the underside. It was obvious that the varnish had afforded no protection to the panel for some time. A large amount of labor would be required to prepare such surfaces for revarnishing.

The purchased floor varnishes, which should be about 25 gallons in length, were inferior to all the 25-gallon varnishes tested.

In the 50-gallon lengths similar differences existed between the natural and modified-phenolic varnishes. Of all the 50-gallon varnishes tested, one containing boea again made the best showing. Not only was it superior to the modified-phenolic varnishes, but also at the end of the six months' period it excelled a varnish containing one of the most expensive 100 per cent phenolic resins available. The tendency of modified-phenolic varnishes to weather by cracking was again revealed in the photomicrographs. The commercial spar varnishes used as controls gave poor performances when compared with either the natural or synthetic varnishes.

In the 50-gallon group the weather resistance of the poorest natural resin varnish was definitely better than that of the varnish from either of two well-known modified-phenolic resins.

In both the 25- and the 50-gallon groups, the natural resin varnishes weathered by such fine checking that the surface required little or no labor to prepare for revarnishing. On the other hand, the weathered modified-phenolic resin varnishes presented surfaces which required laborious preparation prior to refinishing.

Photomicrographs of weathered panels of 15-gallon varnishes did not show the better weathering characteristics of the naturals, as compared with the modified phenolics as well as might be desired. Of the two well-known 100 per cent phenolic resin varnishes, one gave an excellent film while the second gave a film covered by deep checking. This latter was rated as inferior to the natural resin films. An ester gum varnish was the poorest of all the 15-gallon varnishes tested.

In general, the 25-gallon varnishes made from copals (boea, DBB, congo, pontianak) proved to be more durable than those from east india resins (batu, black east india). The east india varnishes were of practically the same quality as the modified-phenolic varnishes. This was not true in the 50-gallon group, for excellent varnishes were obtained with batu and black east india, indicating the adaptability of these low-priced resins to spar varnish formulation.

The only resins to produce more durable films than those obtained from natural resins were two 100 per cent phenolics. A third 100 per cent phenolic varnish was slightly inferior to the boea and manila DBB varnishes.

Ester gum was found to give the poorest films of all the resins tested.

Although boea, along with most of the natural resins, seemed equally suitable for varnishes of any length, congo was found to show to its best advantage in the shorter lengths. This confirmed an opinion already recognized.

Practical Varnish Formulations. In the following collection of miscellaneous varnish formulae, running procedures may or may not be included. If it is lacking, reference should be made to the chapter on thermal processing for recommended treatment. In a number of those formulae which do contain running procedures, the running losses may seem high. In some cases this criticism is merited, for an attempt was made to make these formulae foolproof. For operators unfamiliar with natural resins this was necessary. Experienced men will recognize this and will modify the running according to their own experience. By following the directions given with each formula it will be possible for even inexperienced operators to obtain satisfactory products.

The weather resistance of any varnish is dependent upon the kind of oil used. The summary of tests of various oils is of interest. Twenty-five-gallon varnishes were prepared with oiticica, linseed, perilla, hempseed, fish, soybean, and sunflower oils. As a control, varnishes were also made with an 80 to 20 China wood-linseed oil mixture.

After a ten-month exposure period, it was possible to tabulate those

TABLE LXXVII

COMPARISON OF VARNISHES MADE WITH SAME RESINS AND DIFFERENT OILS

Resins	Oils Giving Best Varnishes
Kauri pale No. 3	1. Oiticica 2. Hempseed 3. China wood-linseed
Boea hard amber	1. China wood-linseed 2. Oiticica 3. Perilla 3. Soybean
Black east india bold scraped	1. China wood-linseed 2. Oiticica 3. Perilla
Hard dark amber congo	1. China wood-linseed 1. Oiticica 3. Perilla 4. Soybean
Manila CBB	1. China wood-linseed 2. Oiticica 3. Perilla 4. Soybean
Manila bold pale chips	1. China wood-linseed 2. Oiticica 3. Perilla 4. Linseed
Manila loba C	1. China wood-linseed 2. Oiticica 3. Perilla 3. Linseed 3. Hempseed
Manila MA	1. China wood-linseed 2. Linseed 3. Oiticica 4. Soybean 4. Sunflower
Pontianak bold scraped	1. Oiticica 2. China wood-linseed 3. Soybean

oils which had made the best showing with each of the resins used (Table LXXVII). The numbers indicate the order of preference; duplicates indicate equal suitability.

In general, the best oils for use in natural resin varnishes appear to be China wood, oiticica, and perilla. Varnishes made from linseed oil were poor. Oiticica oil proved to be almost as good as China wood oil and in a few instances was superior.

Gas-Proofing Natural Resin Varnishes. About 10 per cent of a concentrated phenolic resin (on the weight of natural resin used) is sufficient to gas-proof a natural resin varnish.

Gas-proofness may also be obtained by holding the cook at top heat (560°F.) for a period longer than the normal gelation time of China wood oil. The addition of glycerin permits holding at 560°F. for much longer periods. These periods are roughly proportional to the amount of glycerin added. Gas tests made on varnishes containing glycerin gave good results. The method can be used to produce gas-proof varnishes without danger of gelation. This was checked by an inexperienced operator who merely followed written directions. These formulae, along with test results, are given in Table LXXVIII.

The varnish film from No. 45 was not gas-proof because it had not been held at 560°F. for a long enough period.

Varnishes containing glycerin possessed slightly lower acid numbers than those made without it. The amounts of glycerin added had no harmful effect on the drying time, although the time to set to touch was slightly lengthened. Enamels prepared with these varnishes using lithopone and titanium pigments (about 5 lb. of pigment to a gallon of varnish) showed no increase in consistency at the end of one month.

Floor Varnishes. The statement that old-time floor varnishes using natural resins were more durable than the present-day quick-drying floor finishes made with synthetic resins was investigated by the New England Paint and Varnish Production Club.[4] The naturals were proved to be superior to the synthetics in adhesion and wear resistance. A tribute to the value and place of natural resins is contained in the paper's summary.

> The work of this paper indicates that better wearing floor varnishes can be made by utilizing the good adhesion and wearing qualities of pale east india, batu, pontianak, and esterified congo. Modification of these with low percentages of phenolic resin, excepting heat-reactive phenolics, is desirable to increase the water, alkali, and gas-checking resistance.

[4] *Paint, Oil Chem. Rev.*, 101, No. 23, 80 (1939).

TABLE LXXVIII.—Experimental

Formula No.	40		41	
Oil length (gallons)	25		25	
Composition	lb.	gal.	lb.	gal.
Congo No. 11	100		100	
Philippine manila bold pale				
China wood oil	157	20	157	20
Linseed oil (Kettle bodied—"X" Viscosity)	40	5	40	5
Glycerine	10	1.05	5	0.53
Mineral spirits (150–210°C.)	306	47	306	47
Driers—as metal based on oil content				
Per cent lead	0.5		0.5	
Per cent cobalt	0.01		0.01	
Method of preparation				
Running procedure				
Closed (*C*) or open (*O*) kettle	(*O*)		(*O*)	
Temperature (first stage)	650°F.		650°F.	
Heating time	$1\frac{1}{2}$ hrs.		About	
Temperature maintained	$\frac{1}{2}$ hr.		$1\frac{1}{4}$ hrs.	
Condition of melt	Clean drip		Clean drip	
Oil added	20 gal. C.W.O. + glycerin		20 gal. C.W.O. + glycerin	
Resin and oil heated to	560°F.		560°F.	
Heating time	15–20 min.		15–20 min.	
Held for body	10 min.		8 min.	
Bodied to	Slight string		Slight string	
Check with	5 gal. linseed oil		5 gal. linseed oil	
Cool to	450°F.		450°F.	
Thin with	47 gal. mineral spirits		47 gal. mineral spirits	
Order of drier addition	After thinner		After thinner	
Remarks—% glycerin based on vol. of C.W.O.	5		2.5	
Properties				
Drying time—dust free	$1\frac{1}{2}$ hrs.		1 hr.	
tack free	4 hrs.		4 hrs.	
Gas-proofness	OK		OK	
Resistance to				
Water—cold	98 hrs.—sl. affected		98 hrs.—OK	
boiling	8 hrs.—OK		8 hrs.—OK	
Acid number	8.4		8.8	

PREPARATION OF GAS-PROOF VARNISHES

42		43		44		45	
25		25		25		25	
lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.
100		100		100		100	
157	20	157	20	157	20	157	20
40	5	40	5	40	5	40	5
10	1.05	10	1.05	None	None	7	0.73
306	47	306	47	306	47	306	47
0.5		0.5		0.5		0.5	
0.01		0.01		0.01		0.01	
(*O*)		(*O*)		(*O*)		(*O*)	
600°F.		650°F.		650°F.		650°F.	
1¼ hrs.		1½ hrs.		1½ hrs.		About 1¼ hrs.	
½ hr.		½ hr.		½ hr.			
Clean drip		Clean drip		Clean drip		Clean drip	
						560–580°F.	
						2 lb. glycerin added	
						1 hr.	
20 gal. C.W.O. + glycerin		20 gal. C.W.O. + glycerin		20 gal. C.W.O.		20 gal. C.W.O. + 5 lb. glycerin	
560°F.		560°F.		560°F.		560°F.	
15–20 min.		15–20 min.		15–20 min.		15–20 min.	
10 min.		10 min.		10 min.		5 min.	
Slight string		Slight string		Slight string		Slight string	
5 gal. linseed oil		5 gal. linseed oil		5 gal. linseed oil		5 gal. linseed oil	
450°F.		450°F.		450°F.		450°F.	
47 gal. mineral spirits		47 gal. mineral spirits		47 gal. mineral spirits		47 gal. mineral spirits	
After thinner		After thinner		After thinner		After thinner	
5.0		5		0		3.5	
		Same as No. 1 but prepared by an inexperienced operator					
1½ hrs.		1½ hrs.		1 hr.		1 hr.	
4 hrs.		4 hrs.		4 hrs.		4 hrs.	
OK		OK		Failed		Failed	
98 hrs.—sl. affected		98 hrs.—OK		98 hrs.—OK		98 hrs.—OK	
8 hrs.—OK		8 hrs.—OK		8 hrs.—OK		8 hrs.—OK	
10.3		6.6		12.4		6.6	

The resins tested are listed in Table LXXIX.

TABLE LXXIX

Untreated Resins	Treated Resins	Synthetic Resins
Hard dark amber congo (congo No. 11)	Fused congo (Kopol 501)	Ester gum (acid no. 6–8)
Kauri pale No. 1	Esterified congo (Kopol 500)	Modified phenolic (Amberol F-7)
Pontianak bold scraped	Ester masticated congo (Kopol 502)	100% soluble type phenolic (ST-137 X)
Pale east india bold	Phenolated congo (Beckopol 1400)	100% heat-reactive phenolic (BR-3360)
Black east india bold scraped		
Batu scraped		

These synthetic resins were selected, not because of particular properties, but because they are representative of various classes of resins in common use. It was the New England Club's belief that a study of this type would be rendered worthless if the exact resins used were to be disguised by general terms such as "modified phenolic." By designating the exact resins employed, a varnish formulator may utilize his knowledge of the difference between the many similar resins available and thereby adapt any synthetic resin he wishes to his particular needs.

A series of cooks using fused congo (Kopol 501) were included to determine how a commercially available pre-run congo compared with natural congo No. 11.

A series of cooks using esterified congo (Kopol 500) and a single cook of ester masticated congo (Kopol 502) were included to determine how these types compared with ester gum modifications of natural congo No. 11. Similarly, a single cook of phenolated congo (Beckopol 1400) was included for comparison with phenolic modifications of congo No. 11.

Separate varnishes were prepared for each resin. In addition, two resin blend ratios were selected: 65 per cent synthetic–35 per cent natural, and 35 per cent synthetic–65 per cent natural. The blended varnishes were made by fusing the natural and synthetic resins beforehand.

All varnishes were 25 gallons in oil length, using 20 gallons of China wood oil and 5 gallons of "Q" body linseed oil. Driers equivalent to 0.5 per cent lead, 0.02 per cent manganese, and 0.01 per cent cobalt

naphthenates on the weight of oil were added. Mineral spirits was used as the thinner.

The natural resins were run and cooled prior to use. In this manner, running losses did not disturb the original varnish formula. The exact cooking procedure for each varnish was not recorded, but the following general methods were used:

(*a*) For the 100 per cent natural resin varnishes and also the blends of the natural resins with the synthetics—first heat the resins and all the tung oil to 560°F. in about 1¼ hours, hold if necessary for body and check with the bodied linseed. Thin at 450°F. and add the drier.

(*b*) To make blends of the heat reactive Bakelite 3360 and the natural resins—first heat the natural resin and tung oil to 400°F. Remove from fire and add the heat-reactive phenolic slowly while stirring. When reaction subsides go to 460 or 475°F. and hold for body. Check with linseed and thin.

Several varnishes were made without first running pale east india and black east india. Batu proved to be too troublesome. These cooks are likely to be tricky to handle and care must be exercised to obtain a good solution. It was necessary to run the pale east india to 600°F. in the presence of the oil to obtain a varnish that would not seed out. The unrun black east india cooks were run to a top temperature of 560°F. and seeded out on aging. A higher top temperature of 600°F. may have overcome this as was indicated by the pale east india cook. This method amounts to running the resin in the oil. Opinion is that the time-honored custom of running the resin first, then adding the oils, is preferable.

Discussion of Tests not Included in Tables. In general the viscosities of the varnishes were within the range of "D" to "G" when cooked. Several of the laboratories reported that there was increase in body on aging. The viscosities of the varnishes made with unrun black east india and pale east india were somewhat higher because it was necessary to carry these to a higher temperature.

Non-volatile matter ran within the range of 48 to 52 per cent except for some of the unrun resin cooks, with 45.2 per cent as the lowest reported.

A visual examination of gloss was made of each varnish. All were reported as having a good gloss except the unrun black east india varnish which was reported dull.

Print tests were conducted after 24 hours drying and again after 48 hours drying. All varnishes were reported as showing only slight, or very slight print after 24 hours; after 48 hours all were O.K. or showed

only a faint trace of printing. The varnishes were all dry enough after 24 hours to be suitable for floor varnishes.

The following conclusions were taken directly from the New England Club's report:

> The congo No. 11 varnishes had good adhesion but low wear or abrasion resistance.
>
> The fused congo (Kopol 501) varnishes were duplicates of the congo No. 11 series with the advantage of yielding lighter color, less dirt to contend with, and no gum running loss to take into consideration.
>
> The esterified congo (Kopol 500) varnishes show higher kauri reductions, better resistance to gas-checking, and better initial as well as final wear than the other congo varnishes. The results with esterified congo in combination with ester gum or modified phenolic in particular look very interesting.
>
> The kauri and black east india varnishes had good adhesion but early abrasion failure, similar to congo No. 11 varnishes.
>
> The pontianak varnishes gave the highest initial wear with very good final wear resistance. The adhesion of the pontianak varnishes, however, was only fair. The adhesion was improved by modification with phenolic resins excepting the heat-reactive type.
>
> Pale east india varnishes have good adhesion except when modified with phenolic resins. The initial wear was only fair, but the final wear was the best of the natural resins.
>
> The batu varnishes had good adhesion until the phenolic percentage was increased. The initial wear was fair and final wear good. The color of this series was very dark.
>
> The synthetic varnishes had better color, better water, reagent, and gas-checking resistance. Additions of the synthetic resins to the natural resins generally improved the water, reagent and gas-checking resistance of the naturals. The adhesion of the synthetic varnishes was poor as compared to the natural resin varnishes. Additions of phenolic resins to the natural resins tended to lower the adhesion as well as wear resistance of the naturals unless the phenolic content was kept low. Pontianak and congo were exceptions to this with the 100 per cent soluble type phenolic. The heat-reactive phenolic seemed to lower the adhesion of the natural resins the most and also lowered the wear resistance; bad chipping occurred in nearly all cases where the heat-reactive phenolic was used. Restating the above, the natural resins, particularly pontianak, pale east india, batu and esterified congo improved the adhesion and wear resistance of the synthetic resins.
>
> The alkali resistance of pontianak, congo, and kauri was poor, showing early failure and tended to pull the synthetic resins down to their level in this respect. Esterified congo had fair alkali resistance while batu, black east india and pale east india had fairly good resistance. The tables do not bring out these points as well as they should. Observation of the films dur-

ing the alkali test, however, showed that pontianak, congo, and kauri varnishes were attacked early and were completely dissolved in 3 hours or more, while the other natural resin varnishes were not affected as quickly.

The complete testing results are given in Table LXXX.

The cooking methods used in running the natural resins for this investigation are of interest and are to be found in Table LXXXI.

Skett and Holzberger[5] in continuing the New England Club's work on floor varnishes, found that batu gave slightly better results than pale east india, whereas pontianak was inferior to either of the two resins. Varnishes prepared from the unrun east india resins were slightly better than those from run resins.

The addition of phenolic resins, in general, was found to be detrimental to the properties of adhesion, toughness, abrasion resistance, and stability of drying power. When tested for drying after a five-month aging period, the films of those varnishes containing phenolic resins were tacky after 24 hours, the amount of tackiness being proportional to the quantity of phenolic present. However, the addition of 10 per cent of phenolic resin overcomes any gas-proofing weaknesses and does produce improved resistance to chemicals.

Several tables have been taken from the original article and are presented as Table LXXXII.

The varnishes were 25 gallons in length. All were thinned with mineral spirits to 50 per cent solids. The oil was 80 per cent China wood and 20 per cent linseed. The driers were soluble driers equivalent to 0.5 per cent lead, 0.02 per cent manganese, and 0.01 per cent cobalt as metals on the weight of oil.

Where gas-proofness is not of utmost importance, the varnish No. 178 (Table LXXXIII) is recommended.

Floor varnish formulations are given in Table LXXXIII. If gas-proofness is desired, varnish No. 179 (Table LXXXIII) is excellent.

Although unrun East India resins do not always give products free from "seeding," stable varnishes can be obtained by the procedure given in Table LXXXIII. Actually, the resin is partly run during the 1¼ hour period, but not to the extent normally encountered. The less severe thermal treatment permits the manufacture of lighter varnishes.

Rubbing and Furniture Varnishes. Natural resin varnish films have always been highly prized for the apparent "depth" of their gloss. This property, particularly in the fossil resins, acts to create an illusion that the varnish film is thicker than is actually true. For use as a

[5] A. Skett and J. H. Holzberger, *Paint, Oil, Chem. Rev.*, **102**, No. 21, 24 (1940).

TABLE LXXX

Congo No. 11

Formula No.	Resin Content of Varnishes	Color	Cold Water, 18 hrs.	Hot Water, 15 min.	5% Alkali, 8 hrs.	25% Acetic Acid, 8 hrs.	50% Alcohol, 8 hrs.	Gas-proofness	Skinning (Days)	Drying Dust—Tack—Hard	% Kauri Reduction	Sward Hardness 24 hrs.	Sward Hardness One week	Adhesion Test	Abrasion Test First wear	Abrasion Test Final wear	Remarks on Abrasion and Adhesion
46	Congo 11....100%	13+	Very soft, recovers	Sl. soft and dull, no change	Fails	Soft, recovers	Soft, blisters, recovers	Fails	1	1—3½—overnight	25	34	40	80	25	200	Good adhesion
47	Ester gum....35% Congo 11.....65%	13	Very soft, recovers	Sl. soft, white, remains white	Fails	Blisters, sl. haze, remains	Soft, blisters, recovers	Fails	1	1—3½—overnight	25	34	42	*20	25	200	*Uneven film
48	Ester gum....65% Congo 11.....35%	12	Very soft, recovers	Sl. dull, recovers	Fails	Tiny blisters, recovers	Soft, blisters, recovers	Fails	Edge skin 2 days	1½—4½—overnight	25	42	46	90	25	200	Good adhesion
49	Amb. F-7....35% Congo 11....65%	13	Very soft, recovers	OK	Fails	Tiny blisters, recovers	Soft, blisters, recovers	Fails	Edge skin 16 days	1—4½—overnight	50	40	44	70	25	200	Fair+ adhesion
50	Amb. F-7....65% Congo 11....35%	12	Very soft, recovers	Soft, white, no change	Fails	Tiny blisters, recovers	Soft, blisters, recovers	Fails	Edge skin 7 days	1—4½—overnight	25	42	46	80	25	150	Good adhesion
51	Amb. ST-137X ....35% Congo 11....65%	15+	Very soft, recovers	Sl. soft, no change	Fails	Soft, recovers	Soft, blisters, recovers	Fails	Edge skin 2 days	2—5—overnight	75	38	44	90	25	150	Good adhesion
52	Amb. ST-137X ....65% Congo 11....35%	14	Very soft, recovers	Sl. soft, partial recovery	Fails	Tiny blisters, soft, poor recovery	Soft, blisters, recovers	Fails	Edge skin 2 days	2—7—overnight	100	38	46	85	25	150	Good adhesion
53	Bakelite 3360 ....35% Congo 11....65%	14	Soft, recovers	Sl. soft and sl. white, recovers	Fails	Tiny blisters, soft, recovers	Soft, blisters, recovers	Fails	OK 30 days	1—2½—overnight	50	34	42	45	25	250	Some chipping
54	Bakelite 3360 ....65% Congo 11....35%	13+	Soft, recovers	Sl. soft and sl. white, recovers	Fails	Tiny blisters, soft, recovers	Soft, blisters, recovers	Fails	OK 30 days	1—2½—8	50	42	48	60	25	250	Some chipping

* Uneven coatings—low spots—early abrasion failure.

Fused Congo, Kopol 501

Formula No.	Resin Content of Varnishes	Color	Cold Water, 18 hrs.	Hot Water, 15 min.	5% Alkali, 8 hrs.	25% Acetic Acid, 8 hrs.	50% Alcohol, 8 hrs.	Gas-proofness	Skinning (Days)	Drying Dust—Tack—Hard	% Kauri Reduction	Sward Hardness 24 hrs.	Sward Hardness One week	Adhesion Test	Abrasion Test First wear	Abrasion Test Final wear	Remarks on Abrasion and Adhesion
55	Kopol 501...100%	13	Soft, recovers	Sl. soft, dull, recovers	Fails	Tiny blisters, recovers	Tiny blisters, recovers	Fails	Sl. skin 2 days	2—5—overnight	25	34	40	65	50	200	Good adhesion, fair wear
56	Ester gum....35% Kopol 501....65%	12	Soft, recovers	Sl. dull, soft, fair recovery	Fails	Tiny blisters, recovers	Tiny blisters, recovers	Fails	4	1½—4½—overnight	25	32	46	60	50	200	Good adhesion, fair wear
57	Ester gum....65% Kopol 501....35%	11+	Soft, recovers	Sl. dull, soft, fair recovery	Fails	Blisters, stays sl. soft,	Sl. haze, recovers	Fails	1	1—4—overnight	25	34	46	75	50	100	Good adhesion, fair wear
58	Amb. F-7....35% Kopol 501....65%	12+	Soft, recovers	Soft, fair recovery	Fails	Blisters, stays sl. soft	Tiny blisters, recovers	Fails	Sl. skin 2 days	1½—4—overnight	25	34	46	90	50	100	Good adhesion, even wear
59	Amb. F-7....65% Kopol 501....35%	12	Soft, recovers	Sl. white, soft, stays sl. white	Fails	Blisters, stays sl. soft	Tiny blisters, recovers	Fails	7	1½—3½—overnight	25	34	44	95	50	200	Good adhesion, even wear
60	Amb. ST-137X ....35% Kopol 501....65%	13	Soft, recovers	Sl. dull, sl. soft, recovers	Fails	Tiny blisters, recovers	Tiny blisters, recovers	Fair	2	1½—5½—overnight	25	34	38	95	50	200	Good adhesion, even wear
61	Amb. ST-137X ....65% Kopol 501....35%	15	Soft, recovers	Sl. soft, recovers	Fails	Tiny blisters, recovers	OK	Fair	Sl. skin 2 days	2—5—overnight	75	36	42	85	50	150	Good adhesion, even wear
62	Bakelite 3360 ....35% Kopol 501....65%	13+	Soft, recovers	Sl. white, soft, recovers	Fails	Tiny blisters, recovers	Tiny blisters, soft, recovers	Fails	OK 30 days	1—2½—8	50	38	48	95	25	250	Good adhesion, even wear
63	Bakelite 3360 ....65% Kopol 501....35%	13	Soft, recovers	Sl. white, soft, recovers	Fails	Tiny blisters, recovers	Tiny blisters, soft, recovers	Fair	OK 30 days	1—2½—8	50	42	44	60	25	250	Good adhesion, even wear
64	Ester masticated congo Kopol 502.......100%	11	Soft, recovers	White, soft, stays white	Fails	Tiny blisters, recovers	Tiny blisters, soft, recovers	Fair	1	1—4½—overnight	25	34	40	40	50	150	Fair adhesion, poor wear
65	Phenolated congo Beckopol 1400 ....100%	11	Soft, recovers	Sl. soft, recovers	Fails	Tiny blisters, recovers	Tiny blisters, soft, recovers	Fair	OK 30 days	1—4—overnight	25	32	40	70	50	150	Good adhesion, fair wear

TABLE LXXX (*Continued*)

Esterified Congo, Kopol 500

Formula No.	Resin Content of Varnishes	Color	Cold Water, 18 hrs.	Hot Water, 15 min.	5% Alkali, 8 hrs.	25% Acetic Acid, 8 hrs.	50% Alcohol, 8 hrs.	Gas-proofness	Skinning (Days)	Drying Dust—Tack—Hard	% Kauri Reduction	Sward Hardness		Adhesion Test	Abrasion Test		Remarks on Abrasion and Adhesion
												24 hrs.	One week		First wear	Final wear	
66	Kopol 500...100%	15	Dull, soft, recovers	Sl. dull, soft blisters, blisters stay	Fails	Dull, soft, remains sl. dull	Dull, soft, fair recovery	Fails	1	½—1½—overnight	75	26	50	70	*40	500	Very good adhesion, even wear
67	Ester gum....35% Kopol 500 ...65%	14	Dull, soft, recovers	Sl. soft OK	Fails	Dull, soft, remains sl. dull	Dull, soft, stays dull	Fails	1	1½—4—overnight	50	36	50	75	*40	550	Very good adhesion, even wear
68	Ester gum....65% Kopol 500....35%	13	Dull, soft, recovers	Soft, sl. blisters, blisters stay	Fails	Dull, soft, remains sl. dull	Dull, soft, stays dull	Fair	1	3—12—overnight	25	34	52	65	100	1300	Very good adhesion, even wear
69	Amb. F-7....35% Kopol 500....65%	14	Dull, soft, recovers	Sl. soft OK	Fails	Soft, dull, recovers	Dull, soft, stays dull	Fair	1	1½—4—overnight	50	44	48	70	100	1000	Very good adhesion, even wear
70	Amb. F-7....65% Kopol 500....35%	13	Dull, soft, recovers	Soft, sl. blisters, blisters stay	Fails	Soft, dull, recovers	Dull, soft, stays dull	OK	1	1½—4—overnight	50	42	50	50	125	700	Very good adhesion, even wear
71	Amb. ST-137X ....35% Kopol 500....65%	15	Dull, soft, recovers	Sl. soft OK	Whitens, softens	Soft, dull, recovers	Dull, soft, stays dull	OK	1	1—3—overnight	75	26	48	30	*50	500	Very good adhesion, even wear
72	Amb. ST-137X ....65% Kopol 500....35%	14	Dull, soft, recovers	Sl. soft OK	Whitens, softens	Soft, dull, recovers	Dull, soft, recovers	OK	1	1½—4—overnight	75	26	38	20	*10	500	Fair adhesion, chipped
73	Bakelite 3360 ....35% Kopol 500....65%	12+	Soft, recovers	Sl. soft, sl. white, recovers	White sl. blisters, stays white	Soft, blisters, recovers	Soft, blisters, recovers	OK	2	¾—2½—8	25	38	40	85	25	250	Even wear
74	Bakelite 3360 ....65% Kopol 500....35%	12	Soft, recovers	Sl. soft, sl. white, recovers	Tiny blisters, recovers	Soft, blisters, recovers	Soft, blisters, recovers	OK	Drier soaps on top	¾—2—8	25	40	42	80	25	250	Even wear

Kauri Pale No. 1

75	Kauri No. 1..100%	14+	Soft, white, dull, recovers	Sl. soft, white, dull, fair recovery	Fails	Soft, blisters, recovers	Soft, blisters, recovers	Fails	OK 30 days	1—3½—overnight	25	32	40	50	*25	200	*Abrasion panels were in poor condition as received by testing laboratory which may partly explain the relatively poor results obtained with this series.
76	Ester gum....35% Kauri No.1..65%	13+	Soft, white, recovers	Sl. soft, white, dull, fair recovery	Fails	Soft, blisters, recovers	Soft, blisters, recovers	Fails	2	1—3½—overnight	25	40	48	35	*25	150	
77	Ester gum....65% Kauri No. 1..35%	12+	Soft, waite, recovers	Sl. soft, white, dull, fair recovery	Fails	Soft, blisters, recovers	Soft, blisters, recovers	Fails	1	1—3½—overnight	50	42	50	60	*25	100	
78	Amb. F-7....35% Kauri No. 1..65%	13	Soft, sl. white, recovers	Sl. soft, white, dull, fair recovery	Fails	Soft, blisters, recovers	Soft, blisters, recovers	Fails	2	1—3½—overnight	50	46	50	40	*25	100	
79	Amb. F-7....65% Kauri No. 1..35%	12	Soft, sl. white, recovers	Soft, sl. white, recovers	Fails	Soft, blisters, recovers	Soft, blisters, recovers	Fails	2	1—3½—overnight	65	42	50	75	*25	125	
80	Amb. ST-137X ....35% Kauri No. 1..65%	13+	Soft, sl. white, recovers	Soft, sl. white, recovers	Fails	Soft, blisters, recovers	Soft, blisters, recovers	Fair	2	1—3½—overnight	100	34	50	20	*25	200	
81	Amb. ST-137X ....65% Kauri No. 1..35%	13	Soft, sl. white, recovers	Sl. soft, recovers	Softens, recovers	Soft, blisters, recovers	Soft, blisters, recovers	OK	1	1—3½—overnight	100	38	50	5	*10	75	
82	Bakelite 3360 ....35% Kauri No. 1..65%	14+	Soft, sl. white, recovers	Sl. white, soft, recovers	Fails	Soft, blisters, recovers	Soft, blisters, recovers	Fails	1	¾—2—8	50	42	48	30	25	250	Badly chipped
83	Bakelite 3360 ....65% Kauri No. 1..35%	13	Soft, recovers	Sl. white, soft, recovers	Sl. white, remains white	Soft, blisters, recovers	Soft, blisters, recovers	OK	1	¾—2—8	25	42	48	80	25	250	Badly chipped

* Uneven coatings—low spots—early abrasion failure.

TABLE LXXX (*Continued*)

PONTIANAK BOLD SCRAPED

Formula No.	Resin Content of Varnishes	Color	Cold Water, 18 hrs.	Hot Water, 15 min.	5% Alkali, 8 hrs.	25% Acetic Acid, 8 hrs.	50% Alcohol, 8 hrs.	Gas-proofness	Skinning (Days)	Drying Dust—Tack—Hard	% Kauri Reduction	Sward Hardness 24 hrs.	Sward Hardness One week	Adhesion Test	Abrasion Test First wear	Abrasion Test Final wear	Remarks on Abrasion and Adhesion
84	Pontianak...100%	15	Soft, recovers	Dull, soft, stays sl. dull	Fails	Soft, sl. white, recovers	Dull, soft, recovers	Fails	Sl. edge skin 2 days	1—3½—10	25	44	52	60	450	1350	Fair+ adhesion, chipped
85	Ester gum....35% Pontianak....65%	14+	Soft, recovers	Dull, soft, stays sl. dull	Fails	Soft, sl. white, recovers	Dull, soft, white, recovers	Fails	2	1—4½—12	25	46	54	50	650	1350	Fair+ adhesion, chipped
86	Ester gum....65% Pontianak....35%	13	Soft, recovers	Dull, soft, stays sl. dull	Fails	Soft, sl. white, recovers	Dull, soft, white, recovers	Fails	Sl. edge skin 2 days	1—5½—16	15	36	44	50	650	1200	Fair+ adhesion, chipped
87	Amb. F-7....35% Pontianak....65%	14	Soft, recovers	Dull, soft, stays sl. dull	Fails	Soft, sl. white, recovers	Soft, blisters, recovers	Fails	Sl. edge skin 2 days	1—4—14	25	38	48	60	100	1200	Fair+ adhesion, chipped
88	Amb. F-7....65% Pontianak....35%	13	Soft, recovers	Dull, soft, stays sl. dull	Fails	Soft, sl. white, recovers	Soft, blisters, recovers	Fails	3	1—3½—12	25	38	50	72	350	750	Very good adhesion
89	Amb. ST-137X ....35% Pontianak....65%	15	Soft, recovers	Dull, soft, stays sl. dull	Fails	Soft, sl. white, recovers	Soft, blisters, recovers	Fair	Sl. edge skin 2 days	1—5¼—14	50	36	48	92	100	700	Very good adhesion, even wear
90	Amb. ST-137X ....65% Pontianak....35%	14	Soft, recovers	Dull, soft, stays sl. dull	Fails	Soft, sl. white, recovers	Soft, blisters, recovers	Fair	Sl. edge skin 2 days	¾—5—14	100	30	44	87	600	1100	Very good adhesion, even wear
91	Bakelite 3360 ....35% Pontianak....65%	15+	Soft, recovers	Sl. white, soft, recovers	Fails	Soft, blisters, recovers	Soft, blisters, recovers	Fails	OK 30 days	¾—2½—8	25	38	52	40	25	250	Badly chipped
92	Bakelite 3360 ....65% Pontianak....35%	14	Soft, recovers	Sl. white, soft, recovers	White, stays sl. white	Soft, blisters, recovers	Soft, blisters, recovers	Fair	OK 30 days	¾—2¼—8	25	42	50	50	25	250	Badly chipped

PALE EAST INDIA BOLD

Formula No.	Resin Content of Varnishes	Color	Cold Water, 18 hrs.	Hot Water, 15 min.	5% Alkali, 8 hrs.	25% Acetic Acid, 8 hrs.	50% Alcohol, 8 hrs.	Gas-proofness	Skinning (Days)	Drying Dust—Tack—Hard	% Kauri Reduction	Sward Hardness 24 hrs.	Sward Hardness One week	Adhesion Test	Abrasion Test First wear	Abrasion Test Final wear	Remarks on Abrasion and Adhesion
93	Pale east india 100%	17	Sl. dull, soft, recovers	Sl. dull, soft, recovers	Fails	Soft, recovers	Film lifted	Fails	1	1½—3—overnight	35	34	42	85	100	1500	Good adhesion, even wear
94	Ester gum....35% Pale east india 65%	17	Sl. dull, soft, recovers	Sl. dull, soft, recovers	Fails	Soft, recovers	Blisters, soft, recovers	Fair	1	1½—3—overnight	50	36	44	90	50	1450	Good adhesion, even wear
95	Ester gum....65% Pale east india 35%	15	Sl. dull, soft, recovers	Sl. dull, soft, recovers	Fails	Soft, recovers	Sl. lifting, fair recovery	OK	1	1½—3—overnight	50	40	48	70	50	850	Fair+ adhesion
96	Amb. F-7....35% Pale east india 65%	16	Soft, recovers	Soft, recovers	Fails	Soft, recovers	Film lifted	Fair	1	1½—3—overnight	60	40	48	60	100	1100	Fair+ adhesion
97	Amb. F-7....65% Pale east india 35%	15	Soft, recovers	Soft, recovers	Fails	Soft, recovers	Sl. lifting, fair recovery	Fair	1	1—2—overnignt	75	40	50	80	100	1000	Fair+ adhesion
98	Amb. ST-137X ....35% Pale east india65%	17	Soft, recovers	Soft, recovers	Fails	Soft, recovers	Sl. blisters, soft, recovers	OK	2	2—4—overnight	75	40	48	50	50	850	Chipped
99	Amb. ST-137X ....65% Pale east india35%	16	Soft, recovers	Soft, recovers	Film spotted, fair recovery	Soft, recovers	Sl. blisters, soft, recovers	OK	2	2—4—overnight	100	40	50	40	50	650	Chipped
100	Bakelite 3360, 35% Pale east india 65%	17+	Soft, recovers	Sl. white, soft, recovers	Sl. white, recovers	Soft, recovers	Sl. blisters, soft, recovers	OK	1	¾—1½—8	25	44	54	10	25	300	Badly chipped
101	Bakelite 3360, 65% Pale east india 35%	15+	Soft, recovers	Sl. white, soft, recovers	Sl. white, recovers	Soft, recovers	Sl. blisters, soft, recovers	OK	1	¾—1½—8	50	48	60	30	25	300	Badly chipped
102	Unrun pale east india.....100%	15	Sl. dull, soft, recovers	Sl. dull, soft, recovers	Fails	Soft, recovers	Film lifted	Fails	1	1½—3—overnight	40	38	48	80	150	700	Good adhesion
103	Ester gum....35% Unrun pale east india......65%	14+	Sl. dull, soft, recovers	Sl. dull, soft, recovers	Fails	Soft, recovers	Soft, recovers	Fails	2	1½—3—overnight	45	38	48	75	50	1000	Good adhesion
104	Ester gum....65% Unrun pale east india......35%	14+	Dull, soft, recovers	Dull, soft, recovers	Fails	Soft, recovers	Sl. lifting, fair recovery	Fair	OK 30 days	1½—3—overnight	40	34	44	100	100	950	Excellent, even wear

TABLE LXXX (*Continued*)

Black East India Bold Scraped

Formula No.	Resin Content of Varnishes	Color	Cold Water, 18 hrs.	Hot Water, 15 min.	5% Alkali, 8 hrs.	25% Acetic Acid, 8 hrs.	50% Alcohol, 8 hrs.	Gas-proofness	Skinning (Days)	Drying Dust—Tack—Hard	% Kauri Reduction	Sward Hardness 24 hrs.	Sward Hardness One week	Adhesion Test	Abrasion Test First wear	Abrasion Test Final wear	Remarks on Abrasion and Adhesion
105	Blk. east india 100%	18+	Soft, recovers	Sl. soft, recovers	Fails	Soft, recovers	Sl. soft, recovers	Fails	OK 30 days	4¾—8¼—16	0	28	48	50	25	300	Good adhesion
106	Ester gum....35% Blk. east india 65%	18+	Soft, recovers	Sl. soft, recovers	Fails	Soft, recovers	Sl. soft, recovers	Fails	1	2¾—7—16	25	32	48	40	25	200	Good adhesion
107	Ester gum....65% Blk. east india 35%	18+	Soft, recovers	Sl. soft, recovers	Fails	Soft, recovers	Sl. soft, recovers	Fails	1	4—7½—16	0	30	44	70	25	150	Fair+ adhesion
108	Amb. F-7....35% Blk. eastindia 65%	18+	Soft, recovers	Sl. soft, recovers	Fails	Soft, recovers	Sl. soft, recovers	Fails	1	4½—8—16	25	26	42	95	25	150	Good adhesion, even wear
109	Amb. F-7....65% Blk. eastindia 35%	18+	Soft, recovers	Sl. soft, recovers	Fails	Soft, recovers	Sl. soft, recovers	Fails	1	2½—7¼—16	25	30	44	90	25	250	Good adhesion, even wear
110	Amb. ST-137X ....35% Blk. east india 65%	18+	Soft, recovers	Sl. soft, recovers	Fails	Soft, recovers	Sl. soft, recovers	OK	2	3¼—7¼—16	25	26	44	80	25	150	Good adhesion, even wear
111	Amb. ST-137X ....65% Blk. east india35%	18+	Soft, recovers	Sl. soft, recovers	Softens, whitens	Soft, recovers	Sl. soft, recovers	OK	2	2¼—6¼—16	50	24	40	70	25	100	Fair adhesion
112	Bakelite 3360 35% Blk eastindia65%	18+	Soft, recovers	Sl. soft, recovers	Sl. white, soft, recovers	Tiny blisters, soft, recovers	Tiny blisters, soft, recovers	OK	1	¾—1½—8	25	46	48	5	25	200	Badly chipped
113	Bakelite 3360 65% Blk. eastindia35%	17+	Soft, recovers	Sl. soft, recovers	Sl. white, soft, recovers	Tiny blisters, soft, recovers	Tiny blisters, soft, recovers	OK	1	¾—1½—8	25	50	52	10	25	250	Badly chipped
114	Unrun blk. east india..100%	18+	Soft, recovers	Sl. soft, recovers	Fails	Sl. soft, recovers	Sl. soft, recovers	Fails	2	2¼—6½—16	25	24	40	30	25	250	Good adhesion
115	Ester gum....35% Unrun blk. eastindia..65%	18+	Soft, recovers	Sl. soft, recovers	Fails	Sl. soft, recovers	Sl. soft, recovers	Fails	1	3¾—7¼—16	0	28	34	20	25	250	Good adhesion
116	Ester gum....65% Unrun blk. eastindia..35%	14	Soft, recovers	Sl. soft, recovers	Fails	Sl. soft, recovers	Sl. soft, recovers	Fails	1	4¼—7¾—16	0	36	42	40	25	200	Good adhesion

Batu Scraped

Formula No.	Resin Content of Varnishes	Color	Cold Water, 18 hrs.	Hot Water, 15 min.	5% Alkali, 8 hrs.	25% Acetic Acid, 8 hrs.	50% Alcohol, 8 hrs.	Gas-proofness	Skinning (Days)	Drying Dust—Tack—Hard	% Kauri Reduction	Sward Hardness 24 hrs.	Sward Hardness One week	Adhesion Test	Abrasion Test First wear	Abrasion Test Final wear	Remarks on Abrasion and Adhesion
117	Batu.......100%	18+	Sl. white and soft, recovers	White, recovers	Fails	Sl. white and soft, recovers	Tiny blisters, soft, recovers	Fails	1	1½—2½—overnight	25	32	40	50	50	600	Good adhesion
118	Ester gum....35% Batu........65%	18+	Sl. white and soft, recovers	White, recovers	Fails	Sl. white and soft, recovers	Tiny blisters, soft, recovers	Fails	1	1½—2½—overnight	25	28	40	60	125	800	Good adhesion
119	Ester gum....65% Batu........35%	18	Sl. white and soft, recovers	Sl. white and soft, recovers	Fails	Sl. white and soft, recovers	Tiny blisters, soft, recovers	OK	1	1½—2½—overnight	25	32	40	70	100	750	Good adhesion
120	Amb. F-7....35% Batu........65%	18+	Soft, recovers	Sl. white and soft, recovers	Fails	Sl. white and soft, recovers	Tiny blisters, soft, recovers	Fair	1	1½—2½—overnight	50	38	48	80	75	500	Very good adhesion
121	Amb. F-7....65% Batu........35%	17	Soft, recovers	Sl. white and soft, recovers	Fails	Sl. white and soft, recovers	Tiny blisters, soft, recovers	Fair	1	1½—2½—overnight	50	36	48	95	100	850	Excellent adhesion
122	Amb. ST-137X ....35% Batu........65%	18+	Soft, recovers	Sl. white and soft, recovers	Softens, recovers	Sl. white and soft, recovers	Tiny blisters, soft, recovers	Fair	1	1½—2½—overnight	50	30	42	30	50	800	Fair adhesion, chipped
123	Amb. ST-137X ....65% Batu........35%	18	Soft, recovers	Sl. white and soft, recovers	Softens, recovers	Sl. white and soft, recovers	Tiny blisters, soft, recovers	OK	1	1½—2½—overnight	75	30	40	40	150	600	Fair adhesion, chipped
124	Bakelite 3360 ....35% Batu........65%	18+	Soft, recovers	Sl. white and soft, recovers	Softens, recovers	Tiny blisters, soft, recovers	Tiny blisters, soft, recovers	OK	1	¾—1½—8	25	36	54	20	25	300	Badly chipped
125	Bakelite 3360 ....65% Batu........35%	17	Soft, recovers	Sl. white and soft, recovers	Softens, recovers	Tiny blisters, soft, recovers	Tiny blisters, soft, recovers	OK	1	¾—2—8	50	38	56	40	25	250	Badly chipped

TABLE LXXX (*Continued*)

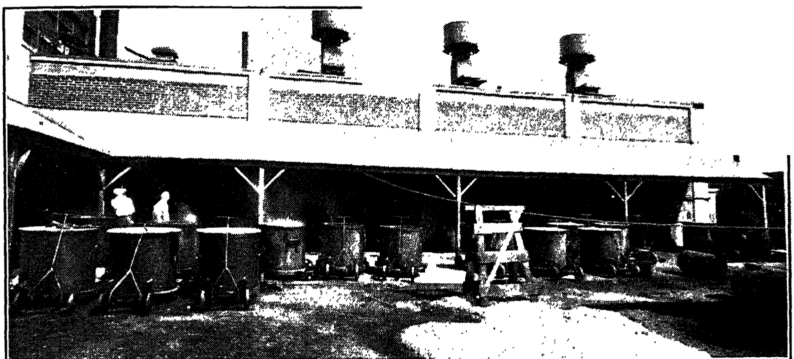
Miscellaneous

Formula No.	Resin Content of Varnishes	Color	Cold Water, 18 hrs.	Hot Water, 15 min.	5% Alkali, 8 hrs.	25% Acetic Acid, 8 hrs.	50% Alcohol, 8 hrs.	Gas-proofness	Skinning (Days)	Drying Dust—Tack—Hard	% Kauri Reduction	Sward Hardness 24 hrs.	Sward Hardness One week	Adhesion Test	Abrasion Test First wear	Abrasion Test Final wear	Remarks on Abrasion and Adhesion
126	Ester gum...100%	11—	Sl. white, dull,soft, recovers	Soft, recovers	Softens, remains soft	Soft, dull, fair recovery	Blisters, soft, fair recovery	Fair	2	1—$3\frac{1}{2}$—overnight	25	28	50	30	*10	*75	*Panel in poor condition as received by testing laboratory
127	Ester gum....65% Bakelite 3360 ....35%	11	Soft, recovers	Sl. white, soft, recovers	Sl. effect, recovers	Softens, blisters, recovers	Softens, blisters, recovers	OK	1	$\frac{3}{4}$—2—8	25	40	46	80	50	250	Even wear
128	Ester gum....35% Bakelite 3360 ....65%	11	Soft, recovers	Sl. white, soft, recovers	OK	Softens, blisters, recovers	Softens, blisters, recovers	OK	1	$\frac{3}{4}$—2—8	50	44	50	70	50	350	Even wear
129	Bakelite 3360 ....100%	10	Soft, recovers	Sl. white, soft, recovers	OK	Softens, blisters, recovers	Softens, blisters, recovers	OK	OK 30 days	$\frac{3}{4}$—2—8	50	46	50	75	25	250	Even wear
130	Amb. F-7...100%	11	Dull, soft, recovers	OK	White, sl. soft, stays white	Soft, dull, recovers	Sl. soft, dull, stays dull	Fails	1	$1\frac{1}{2}$—4—overnight	50	36	48	10	175	1000	Poor adhesion Even wear
131	Amb. ST-137X 100%	12	Soft, recovers	Soft, recovers	Soft	Blisters, recovers	Blisters, recovers	Fair	2	1—2—overnight	100	32	38	20	50	150	Poor wear

rubbing varnish, the oil length usually is kept below 10 gallons, although for furniture varnishes that are not to be rubbed, the length may range from 10 to 25. Table LXXXIV lists a number of high-gloss rubbing varnishes.

Although the varnishes in Table LXXXIV can also be used as furniture varnishes without the necessity for rubbing, it is customary to use varnishes of greater oil length (Table LXXXV).

Baking Varnishes. The color stability of natural resins makes them particularly suited for use in baking finishes either by themselves or in combination with synthetic resins. Batu, black east india, pale east



Courtesy International Nickel Company, Inc.

FIG. 54. Cooling yard of a varnish cook house.

india, and congo are most used. Congo varnishes give harder and more acid-resistant films but lack the alkali resistance of the east india varnishes. Where greater hardness and alkali resistance are desired, phenolic resins may be blended with the naturals. Any discoloration upon baking to which the phenolic resin might be subject is usually not objectionable because of the excellent color retention of the natural resin.

Although natural resin varnishes are dark in bulk, the film is light in color, hard, and glossy. Flexibility may be adjusted by varying the oil length.

Eight- to 12-gallon natural resin baking varnishes prepared with drying or semi-drying oils give satisfactory coatings if baked for one hour at 225-260°F. or for ½ hour at 300°F. China wood oil varnishes of 20- to 25-gallon lengths produce excellent coatings if baked at 260 to 300°F. for one hour or at temperatures above 300°F. for ½ hour. Examples of baking varnishes are given in Table LXXXVI with

TABLE

PREPARATION OF RUN RESINS USED IN

Congo No. 11			Pontianak			Kauri		
Schedule			*Schedule*			*Schedule*		
Min.	Temp. °F.	Procedure	Min.	Temp. °F.	Procedure	Min.	Temp. °F.	Procedure
55	600	Pull	60	600–575	Pull and breath‡	55	600	Pull from fire
10	625	Pull	15	625–600	Pull from fire	15	635	Clean drip, pull, and let cool to 500°F.; dip into pan
15	640	Pull and whip down the foam	10	625–600	Pull			
10	660	Hold	10	640	Clean drip—pull and let cool			
15	660	Clean drip, pull, and cool to 500°F.; dip into pans						
105		Total time on fire	95		Total time on fire	70		Total time on fire
Loss 23.5%			Loss 38%			Loss 28%		
Remarks			*Remarks*			*Remarks*		
Headed* in the kettle and required whipping.† This left a deposit of resin on the sides of the kettle which could not be removed, resulting in a high loss. An open kettle was used until the final heat of 660°F. when a cover was used to prevent flashing of the batch. Cooled to 500°F. before dipping to prevent a flash while dipping.			Pontianak also headed badly in the kettle and had to be whipped. Owing to deposits on sides of kettle the loss recorded is high.			Owing to deposit on sides of kettle the loss recorded is high.		

* Headed is the varnish man's term for excessive foam which tends to rise in the kettle.

† Whipping means that a flexible metal rod was used to beat down the foam and keep the batch in the kettle.

recommended baking schedules. Batu, black east india, pale east india, pontianak, boea, and congo can all be used with equal facility.

In the 8-gallon example, kettle-bodied perilla oil may be substituted for the China wood oil without change in the properties of the varnishes. In the 12- and 25-gallon examples, China wood or perilla may replace the soybean without change in varnish preparation or properties.

Crystal finishes take advantage of gas checking of certain resin-oil combinations to give a frosted appearance upon baking in a fouled oven. The frosting effect takes the form of a main framework of wrinkles of a more or less geometrical pattern, with each figure filled with much finer wrinkles running in all directions.

An example of a crystal varnish is given in Table LXXXVI.

Spar Varnishes. In a spar varnish, the chief requirement is a film possessing sufficient flexibility to withstand the contractions and ex-

LXXXI

NEW ENGLAND FLOOR VARNISH STUDY

Pale East India			Black East India			Batu		
Schedule			*Schedule*			*Schedule*		
Min.	Temp. °F.	Procedure	Min.	Temp. °F.	Procedure	Min.	Temp. °F.	Procedure
40	600	Pull and stir	50	600	Pull and stir	40	600	Pull and stir
5	600	Pull and stir	10	600	Pull and stir	20	625	Clean drip, pull, and let cool to 500°F., then dip into pan
5	630	Clean drip from paddle, pull from fire; cool to 500°F. and dip into pan	10	640	Clean drip from paddle; pull and let cool to 500°F. before dipping			
50	Total time on fire		70	Total time on fire		60	Total time on fire	
Loss	15%		Loss	24%		Loss	25%	
Remarks			*Remarks*			*Remarks*		
Actual loss was under 15%.			Actual loss was under 24%.			Actual loss was under 25%.		

‡ Breathing a batch means a short period of time allowed to permit escape of occluded air and gases to prevent excessive foaming.

pansions incidental to weathering. For this reason, long-oil varnishes are demanded, the usual length being 50 gallons.

Formula 190 (Table LXXXV) represents a spar or outdoor varnish which has demonstrated its worth in actual testing.

In a similar manner, the 50-gallon varnishes shown in Table LXXXVII may be prepared and used satisfactorily as outdoor finishes.

Properties. These varnishes surpassed modified-phenolic varnishes in weathering tests. All possess the characteristic even weathering of natural varnish films.

Even in varnishes of 25-gallon lengths, satisfactory outdoor varnishes can be made with these resins. For such lengths, the oil contents of the preceding varnishes would be halved.

Congo does not show to its best advantage in long-oil varnishes. Boea, manila DBB, pale east india, black east india, and batu all give more durable films in varnishes of this length. The last two are em-

TABLE LXXXII.—

Formula No.	Resin Composition						
	Run pale east india Macassar nubs	Run batu scraped	Run pontianak nubs	Phenolic (Amberol ST-137X)	Ester gum "C"	Unrun pale east india Macassar nubs	Unrun batu scraped
132	100	...	...	...	...	...	...
133	...	100	...	...	...	...	...
134	...	...	100	...	...	...	...
135	65	...	...	35	...	...	...
136	75	...	...	25	...	...	...
137	90	...	...	10	...	...	...
138	75	...	10	15	...	...	...
139	90	...	10	...	...	...	...
140	75	...	...	15	10	...	...
141	75	...	...	...	25	...	...
142	90	...	...	...	10	...	...
143	75	25	...	...	...	...	...
144	25	75	...	...	...	...	...
145	75	...	25	...	...	...	...
146	25	...	75	...	...	...	...
147	...	75	25	...	...	...	...
148	...	25	75	...	...	...	...
149	25	50	25	...	...	...	...
150	25	25	50	...	...	...	...
151	65	25	...	10	...	...	...
152	50	25	...	25	...	...	...
153	25	50	...	25	...	...	...
154	80	...	10	10	...	...	...
155	65	...	25	10	...	...	...
156	50	...	25	25	...	...	...
157	25	...	50	25	...	...	...
158	...	50	25	25	...	...	...
159	...	25	50	25	...	...	...
160	...	...	...	...	...	100	...
161	...	...	...	...	...	...	100
162	...	...	...	25	...	75	...
163	...	...	...	10	...	90	...
164	...	...	...	...	25	75	...
165	...	...	...	...	10	90	...
166	...	...	...	25	...	...	75
167	...	...	...	10	...	...	90
168	...	...	...	...	25	...	75
169	...	...	...	...	10	...	90
170	...	75	...	...	25	...	...
171	...	90	...	...	10	...	...
172	...	75	...	25	...	...	...
173	...	90	...	10	...	...	...

* Rating of panel based on general appearance after washing. Ratings 1 to 42, with 1 for best appearance, 42 for worst appearance.

FLOOR VARNISHES

Results of Pounding Test					Results of Sliding Abrasion Test, Dry—Number of Rubs to Failure	
Per cent wear (film area left)	Adhesion	Type failure	Condition after washing	Rating,* appearance after washing	First showing	80 per cent gone
45	Very poor	Sl. chip	Very dirty	39	250	725
75	Good	Very sl. chip	Very dirty	20	350	1,050
50	Poor	Sl. chip	Dirty	37	300	750
65	Fair	Sl. chip	Fairly clean	26	350	1,000
35	Very poor	Bad chip	Dirty	42	260	700
55	Poor	Some chip	Dirty	36	325	825
60	Fair	Bad chip	Dirty	32	350	900
50	Poor	Bad chip	Very dirty	38	375	775
65	Fair	Some chip	Dirty	28	400	1,000
60	Fair−	Bad chip	Very dirty	33	350	1,200
40	Very poor	Very sl. chip	Dirty	41	300	1,100
75	Fair+	Some chip	Very dirty	21	380	1,000
92	Very good	Very sl. chip	Fairly clean	6	450	1,400
65	Fair	Some chip	Clean	25	370	1,150
55	Poor	Some chip	Clean	35	350	800
60	Poor	Some chip	Clean	29	300	950
40	Very poor	Bad chip	Clean	40	500	1,200
85	Good	Sl. chip	Dirty	13	475	1,300
70	Fair+	Very sl. chip	Fairly clean	23	250	950
80	Good	Sl. chip	Fairly clean	17	350	1,050
85	Good−	Sl. chip	Fairly clean	12	450	1,350
55	Poor	Some chip	Clean	34	200	950
60	Poor	Bad chip	Clean	30	350	1,150
75	Fair	Bad chip	Fairly clean	19	700	1,450
60	Poor	Bad chip	Fairly clean	31	425	1,100
85	Good	Sl. chip	Fairly clean	11	525	1,350
70	Fair	Bad chip	Clean	22	550	1,150
70	Fair	Bad chip	Dirty	24	500	1,100
65	Poor	Bad chip	Fairly clean	27	480	1,150
90	Very good	Even wear	Fairly clean	9	375	1,100
80	Good	Sl. chip	Clean	14	400	900
90	Very good	Sl. chip	Clean	8	350	850
92	Very good	Sl. chip	Clean	5	300	1,100
98	Excellent	Even wear	Clean	2	275	1,150
80	Good	Sl. chip	Clean	15	300	1,050
90	Very good	Even wear	Clean	7	250	1,000
100	Excellent	Even wear	Clean	1	525	1,175
90	Good+	Sl. chip	Clean	10	350	1,050
75	Good−	Sl. chip	Clean	18	350	900
80	Good	Sl. chip	Clean	16	350	950
92	Very good	Even wear	Clean	3	200	1,000
95	Very good+	Very sl. chip	Clean	4	150	850

TABLE LXXXIII.

Formula No.	174		175	
Oil length (gal.)	15		20	
Composition	lb.	gal.	lb.	gal.
Congo No. 11	100		100	
Boea medium dark				
Black east india bold scraped				
Batu scraped				
Ester gum				
100% Phenolic resin				
China wood oil	95	12	108	15
Linseed oil (kettle-bodied—"B" viscosity)	24	3	40	5
Linseed oil (kettle-bodied—"R-S" viscosity)				
Mineral spirits (150–210°C.)	175	27	214	33
Driers—as metal based on oil content				
Per cent lead	0.5		0.5	
Per cent cobalt	0.02		0.02	
Per cent manganese	0.01		0.01	
Method of preparation				
Running procedure				
Closed (C) or open (O) kettle	(O)		(O)	
Temperature (first stage)	650°F.		650°F.	
Heating time	As short as possible		As short as possible	
Temperature maintained				
Condition of melt	No foam. Clean drip.		No foam. Clean drip.	
Temperature (second stage)				
Temperature maintained				
Condition of melt				
Preparation of varnish				
Oil added	12 gal. C.W.O.		15 gal. C.W.O.	
Preheating temperature				
Resin and oil brought to				
Oil added				
Resin and oil heated to	560°F.		560°F.	
Held for body	To desired viscosity		To desired viscosity	
Check with	3 gal. linseed oil		5 gal. linseed oil	
Cool to	400°F.		400°F.	
Thin with	27 gal. mineral spirits		33 gal. mineral spirits	
Order of drier addition	After thinner		After thinner	
Properties				
Drying time—dust free				
—tack free	4 hrs.		4 hrs.	
Color (Gardner)				
Viscosity—(Gardner-Holdt)				
Gloss				
Gas-proofness				
Resistance to cold water				

Floor Varnishes

176		177		178		179	
25		25		25		25	
lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.
100							
		100					
				75–90		90	
				25–10			
						10	
157	20	157	20	157	20	157	20
				40	5	40	5
40	5	40	5				
297	46	297	46	297	46	297	46
0.4		0.4		0.5		0.5	
0.03		0.03		0.01		0.01	
0.01		0.01		0.02		0.02	
				Resin heated with 5 gal. C.W.O.		Resin heated with 5 gal. C.W.O.	
(C)		(C)		(O)		(O)	
625°F.		610°F.		600–610°F.		600–610°F.	
1 hr.		1 hr.		1½ hrs.		1½ hrs.	
1 hr.		Cooled to 480°F.					
Oil soluble				No foam		No foam	
		625°F.					
		1 hr.		10 min.		10 min.	
		Oil soluble		A clear bead on cooling		A clear bead on cooling	
20 gal. C.W.O.		20 gal. C.W.O.					
400°F.		400°F.					
560°F.		560°F.		520°F.		520°F.	
5 gal. linseed oil		5 gal. linseed oil		15 gal. C.W.O.		15 gal. C.W.O.	
518°F.		518°F.		560°F.		560°F.	
To desired viscosity		To desired viscosity					
				5 gal. linseed oil		5 gal. linseed oil	
450°F.		450°F.		400°F.		400°F.	
46 gal. mineral spirits		46 gal. mineral spirits		46 gal. mineral spirits		46 gal. mineral spirits	
After thinner		After thinner		After thinner		After thinner	
1 hr.		1 hr.					
3 hrs.		3 hrs.					
15		18+					
G		G					
High		High					
				Not completely gas-proof		Gas-proof	
Good		Good					

TABLE

	Rubbing			
Formula No.	180		181	
Oil length (gal.)	8		8	
Composition	lb.	gal.	lb.	gal.
Congo No. 11	100			
Batu scraped				
Boea medium dark			100	
Black east india bold scraped				
China wood oil	63	8	63	8
Linseed oil (kettle-bodied—"B" viscosity)				
Mineral spirits (150–210°C.)	195	30	195	30
Driers—as metal based on oil content				
Per cent lead	0.4		0.4	
Per cent manganese	0.03		0.03	
Per cent cobalt	0.01		0.01	
Method of preparation				
Running procedure				
Closed (C) or open (O) kettle	(O)		(C)	
Temperature (first stage)	650°F.		625°F.	
Heating time	1 hr.		1 hr.	
Temperature maintained	$1\frac{3}{4}$ hrs.		Cooled to 520°F.	
Condition of melt	Oil soluble			
Temperature (second stage)			610°F.	
Temperature maintained			1 hr.	
Condition of melt			Oil soluble	
Preparation of varnish				
Oil added	8 gal. C.W.O.		8 gal. C.W.O.	
Preheating temperature			400°F.	
Resin and oil brought to				
Heating time				
Temperature maintained				
Oil added				
Resin and oil heated to	560°F.		580°F.	
Held for body	To desired viscosity		To desired viscosity	
Check with				
Cool to	400°F.		400°F.	
Thin with	30 gal. mineral spirits		30 gal. mineral spirits	
Order of drier addition	After thinner		After thinner	
Properties				
Drying time—dust free	1 hr.		1 hr.	
—tack free	3 hrs.		3 hrs.	
Color—(Gardner)	18		16	
Viscosity—(Gardner-Holdt)	F		G	
Gloss	High		High	
Gas-proofness	OK		OK	
Resistance to cold water	OK		High	

LXXXIV

Varnishes		Flat Varnishes					
182		183		184		185	
8		8		20		15	
lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.
		108		100		100	
100							
63	8			157	20	118	15
		64	8				
195	30	156	24	292	45	215	33
0.4		0.5		0.5		0.5	
0.03		0.01		0.01		0.01	
0.01		0.02		0.02		0.02	
						None	
(C)		(O)		(O)			
610°F.		450°F.		450°F.			
1 hr.		1 hr.		45 min.			
Cooled to 480°F.		Until completely melted		Until completely melted			
625°F.							
1 hr.							
Oil soluble		Loss in weight about 7.5 per cent					
8 gal. C.W.O.		8 gal. linseed oil		20 gal. C.W.O.			
400°F.							
		500°F.		480°F.		500°F.	
		As short as possible		As short as possible		35 min.	
						10 min.	
560°F.							
To desired viscosity							
400°F.		400°F.		400°F.		400°F.	
30 gal. mineral spirits		24 gal. mineral spirits		45 gal. mineral spirits		33 gal. mineral spirits	
After thinner		After thinner		After thinner		After thinner	
1 hr.				Dries hard and flexible overnight			
4 hrs.							
18+							
E							
High							
OK							
High							

TABLE LXXXV

	Furniture Varnishes								Boea Spar Varnish	
Formula No.	186		187		188		189		190	
Oil length (gal.)	15		15		15		15		50	
Composition	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.
Congo No. 11	100		100							
Boea medium dark					100				100	
Black east india bold scraped							100			
China wood oil	118	15	94	12	94	12	94	12	295	37.5
Linseed oil (pale bodied—"R-S" viscosity)			24	3	24	3	24	3	101	12.5
Mineral spirits (150–210°C.)	214	33	221	34	221	34	221	34	476	31
Driers—as metal based on oil content										
Per cent lead	0.5		(17.2 lb. cryst. lead acetate)		(17.2 lb. cryst. lead acetate)		(17.2 lb. cryst. lead acetate)		0.4	
Per cent cobalt	0.01		0.01		0.01		0.01		0.009	
Per cent manganese	0.01		0.03		0.03		0.03		0.03	
Method of preparation										
Running procedure										
Closed (C) or open (O) kettle	(C)		(O)		(C)		(C)		(C)	
Temperature (first stage)	600°F.		650°F.		625°F.		610°F.		625°F.	
Heating time	1 hr.		1 hr.		1 hr.		1 hr.		1 hr.	
Temperature maintained	Until foam subsides		1 hr.		1 hr.		Cooled to 500°F.		1 hr.	
Condition of melt			Oil soluble		Oil soluble				Oil soluble	
Temperature (second stage)	650°F.						625°F.			
Temperature maintained	Until foam subsides									
Condition of melt	Oil soluble						Oil soluble			
Preparation of varnish										
Oil added	15 gal. C.W.O.		12 gal. C.W.O.		12 gal. C.W.O.		12 gal. C.W.O.		37.5 gal. C.W.O.	
Preheating temperature			400°F.		400°F.		400°F.			
Resin and oil brought to			560°F.		560°F.		560°F.			
Oil added			3 gal. lin. oil + Pb acetate		3 gal. lin. oil + Pb acetate		3 gal. lin. oil + Pb acetate			
Resin and oil heated to	560°F.		518°F.		518°F.		518°F.		560°F.	
Held for body	To desired body		½ hr. (approx.)		½ hr. (approx.)		½ hr. (approx.)		To desired viscosity	
Check with									12.5 linseed oil	
Cool to	400°F.		480°F.		480°F.		480°F.		420°F.	
Thin with	33 gal. mineral spirits		34 gal. mineral spirits		34 gal. mineral spirits		34 gal. mineral spirits		31 gal. mineral spirits	
Order of drier addition	After thinner		Mn and Co after thinner		Mn and Co after thinner		Mn and Co after thinner		After thinner	
Properties										
Drying time—dust free			1 hr.		1 hr.		1 hr.			
—tack free			3 hrs.		3 hrs.		4 hrs.			
Color—(Gardner)			17		17		18+			
Viscosity—(Gardner-Holdt)			E		E		E			
Gloss			High		High		High			
Gas-proofness			OK		OK		OK			
Resistance to cold water			High		High		High			
Weatherability									Excellent	

TABLE LXXXVI

	Baking Varnishes								Crystal Varnish	
Formula No.	191		192		193		194		195	
Oil length (gal.)	8		12.8		20		25		26	
Composition	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.
Thermally processed resin	100		100		100		100		100 (Congo)	
China wood oil	62.8	8	75	9.5	118	15	157	20	165	21
Soybean oil (kettle-bodied)			25	3.3	39	5	39	5		
Perilla oil (kettle-bodied)										
Linseed oil (kettle-bodied—"B" viscosity)									40	5
Mineral spirits (150–210°C.)	161	24.8	198	30.5	257	39.6	297	45.7	306	47
Driers—as metal based on oil content										
Per cent lead									0.25	
Per cent cobalt									0.01	
Method of preparation										
Running procedure										
Closed (C) or open (O) kettle									(O)	
Temperature (first stage)									650°F.	
Heating time									1¼ to 1½ hrs.	
Temperature maintained									Until foam subsides	
Condition of melt									Oil soluble Cool to 540°F.	
Oil added			9.5 gal. C.W.O.		15 gal. C.W.O.		20 gal. C.W.O.		21 gal. C.W.O.	
Preheating temperature									500°F.	
Resin and oil heated to	560°F.		580°F.		580°F.		580°F.		550°F.	
Heating time	1¼ hrs.		1¼ hrs.		1¼ hrs.		1¼ hrs.			
Held for body	7 min.		If necessary		If necessary		If necessary		Check immediately	
Check with			3.3 gal. soybean oil		5 gal. soybean oil		5 gal. soybean oil		5 gal. linseed oil	
Cool to	400°F.		400°F.		400°F.		400°F.		400°F.	
Thin with	24.8 gal. mineral spirits		30.5 gal. mineral spirits		39.6 gal. mineral spirits		45.7 gal. mineral spirits		47 gal. mineral spirits	
Order of drier addition									After thinner	
Properties										
Baking schedule										
Temperature (first stage)	225–260°F.		225–260°F.		225°F.		225–260°F.		For crystal effect bake in a fouled oven	
Time	1 hr.		1 hr.		1½ hrs.		1 hr.			
Temperature (second stage)	300°F.		300°F.		260°F.		300°F.			
Time	½ hr.		½ hr.		1 hr.		½ hr.			
Temperature (third stage)					300°F.					
Time					½ hr.					

TABLE LXXXVII

Formula No.	Pounds	Resin	China Wood Oil (*Gallons*)	Linseed Oil, Kettle-Bodied "B" Viscosity (*Gallons*)
196	100	Brown kauri No. 1	45	5
197	100	Black east india, bold scraped	45	5
198	100	Batu, bold	45	5
199	100	Pale east india, bold	45	5
200	100	Manila DBB	37.5	12.5

Plus thinners and driers as in formula 190.
Procedure. Same as for varnish 190.

ployed in inexpensive spar varnishes whose durability far exceeds that of ester gums and, with a lesser degree of superiority, that of the modified phenolics.

Flat Oil Varnishes. Batu is most suitable for the preparation of flat oil varnishes.

The processing method determines the film flatness. The lower the processing temperature the lower the gloss. Temperatures must be chosen which produce solubility at the least sacrifice of flatness. This point appears to be 500°F. Temperatures higher than this will tend to increase the gloss of the film. Table LXXXIV contains examples of flat varnishes.

Semi-gloss varnishes may be obtained by blending a flat varnish with high-gloss varnishes.

Although the results are not so satisfactory as those from formulae 183 and 184, flat varnishes can be prepared by eliminating the processing operation and heating resin and oil together (formula 185).

Wrinkle Finishes. Natural resins were the first to be used in the preparation of the so-called "wrinkle finishes." These are based upon the formation, as a result of rapid drying, of a hard skin over a less oxidized inner film. This surface film increases in volume (owing to absorption of the semi-liquid beneath) and expands laterally. The less oxidized portion of varnish beneath the skin, being of lower viscosity flows into the folds produced by expansion of the outer film where it too eventually hardens. The general effect obtained is that of a level surface covered with ridges projecting from the surface and running in all directions. The entwined ridges enclose flat areas of various sizes and shapes.

The finishes may be pigmented to any desired shade. Being hard, attractive, easy-to-grip, and durable they are applied to all sorts of objects that are subjected to hard wear or repeated handlings. They are used mostly for metal articles such as cameras and photographic apparatus, radio accessories, scientific apparatus and instruments, metal containers, tool handles, and phonograph pick-ups. Although wrinkle finishes collect dust, they have the advantage of showing no fingerprints or superficial scratches.

The chief consideration in the formulation of wrinkle finishes is the selection of oil. Raw and blown linseed oils give poor results, wrinkles being obtained only when applied in thick films. Raw perilla and raw China wood oils can be made to produce some wrinkling when dried under proper conditions, but blown China wood oil wrinkles readily. Semi- and non-drying oils have no wrinkling properties.

To secure hardness, toughness, better adhesion, and durability, resins are used. The smaller the amount of resin or bitumen, the smaller the wrinkle and vice versa. The proportion of oil to resin is generally controlled over a rather narrow range of 7½ to 17 gal. per 100 lb. of resin. Insufficient oil will not produce wrinkling, although too much promotes irregularity of finish.

The limits[6] for best wrinkling are: blown China wood oil, 6–18-gallon length; raw China wood oil, 8–25-gallon length; blown perilla oil, 10–30-gallon length; blown linseed oil, 14–35-gallon length.

The relative rates of wrinkling power were: blown China wood oil, 5;[7] raw China wood oil, 6½; blown perilla oil, 8; blown linseed oil, 12.

Wrinkle finishes are usually applied by spraying or dipping. Brushing gives unsatisfactory films. Thin films give finer wrinkles, whereas thicker films produce more pronounced effects.

Although these finishes can be made to air-dry, the size, shape, and toughness of the wrinkle can be uniformly controlled only by baking in a closed oven, gas-heated inside, at temperatures ranging from 150 to 400°F. Higher temperatures produce better wrinkles and harder films. Black and dark colors are usually baked at a high temperature for a short period, whereas lower temperatures and longer periods are used for light colors to prevent discoloration. The baking temperature also depends upon the wrinkling power of the oil used. For example, blown China wood oil requires a temperature only about three-fourths that needed for the less powerful blown perilla or linseed oils.

[6] Chadeloid Chem. Co., U. S. Patent 1,864,763 (1932).

[7] Low values indicate high wrinkling power.

An early patent[8] recommended the formula 201 listed in Table LXXXVIII, using Congo resin. The film when applied is subjected to forced drying at baking temperatures, producing a wrinkled effect. In addition to congo, the following natural resins were also included in the patent as being suitable: damar, kauri, manila, elemi, mastic, congo ester, and manila ester. Nitrocellulose, gilsonite, and rosin were

Courtesy International Nickel Company, Inc.

FIG. 55. Large size varnish kettle.

found to inhibit wrinkling as their amounts were increased. Large amounts of rosin also cause irregularity. Additional examples as given in the patent are listed in Table LXXXVIII, formulae 202 to 204 inclusive.

Another means of controlling the wrinkle lies in the type and amount of thinner used. Low-boiling (below 325°F.), easily volatilized solvents are the most desirable. High-boiling solvents tend to form fine wrinkles. Formula 205, Table LXXXVIII, illustrates a fine-wrinkle varnish formula. Other examples are formulae 206 to 215, inclusive, Table LXXXVIII.

At least 50 per cent of the oils contained in a wrinkle varnish must be of the wrinkling type. Formula 216, Table LXXXVIII, illustrates

[8] U. S. Patent 1,689,892 (1928).

TABLE LXXXVIII

Formula No.	Resins: Congo (lb.)	Resins: Rosin (lb.)	Resins: Kauri (lb.)	Driers: Red lead (oz.)	Driers: Manganese borate (oz.)	Driers: Manganese oxide (oz.)	Driers: Lead linoleate (oz.)	Driers: Cobalt linoleate (oz.)	Driers: Cobalt acetate (oz.)	Driers: Litharge (oz.)	Oils: Raw China wood oil (gal.)	Oils: Blown China wood oil (gal.)	Oils: Blown perilla oil (gal.)	Oils: Blown linseed oil (gal.)	Oils: Blown soybean oil (gal.)	Oils: Rapeseed oil (gal.)	Thinners and Solvents: Dibutyl phthalate (gal.)	Thinners and Solvents: Toluol (gal.)	Thinners and Solvents: Light naphtha (gal.)	Thinners and Solvents: Heavy naphtha (gal.)	Thinners and Solvents: Turpentine (gal.)	Thinners and Solvents: Xylol (gal.)	Remarks
201	25	1¼	..	7	3	..	..	..	..	..	⅝	1⅝	..	..	..	..	..	5¾	..	..	..	..	
202	25	1¼	..	7	3	..	..	..	..	..	⅝	1¼	..	..	..	..	..	1¼	5½	..	..	..	
203	25	1¼	..	7	3	..	..	..	..	..	⅝	2⅜	..	..	..	..	..	8	..	..	..	..	
204	25	1¼	..	7	3	..	..	..	..	..	⅝	3¾	..	..	..	..	..	7	..	..	..	..	
205	25*	1¼	..	7	3	..	..	..	..	..	⅝	⅝	..	..	..	..	..	..	¾	4¾	1¼	..	
206	100†	4	..	56	..	32	..	..	..	..	10	..	..	..	..	..	..	32	10	..	..	..	
207	100†	..	..	80	..	40	..	..	..	..	..	..	..	25	..	..	..	18	10	..	..	..	
208	100†	..	..	40	20	..	..	..	..	..	..	..	..	15	..	..	..	19	..	..	5	..	Finish quite even, showing well-defined wrinkles.
209	100†	..	..	..	12	..	72	..	8	..	..	..	10	..	..	..	..	5	..	..	..	..	Fairly uniform results.
210	..	4	100†	..	24	..	160	..	20	..	2½	22½	..	..	..	..	..	22	5	..	..	..	Uniform wrinkles quite close together and fine in texture.
211	50†	5	50	48	20	..	..	..	52	..	2½	3¼	3¾	..	..	..	..	17	5	..	..	..	Good wrinkling effect.
212	100†	..	..	..	16	..	..	..	..	48	..	..	6¼	7½	..	..	..	20	2½	..	2½	..	Satisfactory wrinkling effect.
213	100†	..	..	32	12	..	..	20	..	..	1¼	6	2½	3	2½	..	..	17	4	..	..	..	Very pronounced wrinkles on baking.
214	..	..	100†	32	16	..	..	..	8	..	..	..	10	10	3	..	..	..	..	..	..	22	Fairly coarse wrinkling.
215	100†	4	..	32	16	..	..	..	..	..	2	5	..	2	..	..	..	5	20	..	..	..	Very good wrinkling effect.
216	100†	4	..	28	12	..	..	..	..	..	2½	6½	..	..	4	..	..	17	5	..	..	..	
217	100‡	5	..	22	12	..	..	32	..	..	2½	11½	..	..	5	..	..	20	5	..	..	..	Pronounced wrinkles. Size can be modified by allowing the film to air-dry partly before baking.
218	100‡	5	..	28	12	..	..	32	..	..	2½	9¾	..	..	5¾	..	..	19	5	..	..	..	Fairly fine wrinkling.
219	100‡	..	..	..	..	8	..	80	..	32	2½	15½	..	..	16	..	..	24	5	..	..	..	Particularly good wrinkling.
220	100‡	5	..	28	12	..	..	..	32	..	2½	6½	..	3½	..	1¾	1¾	22	5	..	..	..	Well-defined and fairly coarse wrinkles.

* U. S. Patent 1,689,892 (1928) † U. S. Patent 1,864,763 (1932) ‡ U. S. Patent 1,831,323 (1931)

the use of a non-wrinkling oil. Formulae 217 to 220 are for flexible wrinkle finishes for paper, metal foil, cloth, etc.

In the baking of the foregoing wrinkle finishes, various combinations of time and temperature may be used. Higher temperatures promote better wrinkling and harder films. Satisfactory finishes may be obtained at 180°F. for 5 hours, 200°F. for 3 hours, 250°F. for 2 hours, 300°F. for 1½ hours, or 400°F. for ¾ hour.

The amount and nature of the driers are important. Cobalt gives the greatest surface wrinkling, zinc the least, and lead and manganese an intermediate effect. Natural resins may also be used in combination with modified phenolics,[9] or alkyds,[10] in wrinkle finishes.

Damar Oil Varnishes. Damar oil varnishes possess inherent softness. The inclusion of a heat-reactive phenolic resin reduces softness. When 3 parts of damar and 1 part of heat-reactive phenolic resin are melted together, the resulting resin mixture has a softening point of 212°F. as compared with the usual damar softening point of 159 to 170°F.

These mixtures can be prepared by melting the damar, then, while stirring, slowly adding the phenolic resin. The time at 400°F. is about 30 minutes. At 450°F. the combination can be effected in 5 minutes.

Usually, it is not necessary to use so large a proportion of phenolic resin, as much smaller amounts are sufficient to eliminate tackiness. The damar-phenolic mixture has much better color retention than the phenolic resin alone.

The hardness of damar may also be increased by incorporation with other hard resins such as the ordinary phenolic resins or those of the maleic anhydride type. With these resins somewhat larger amounts are necessary to secure the same results. When used in the preparation of oil varnishes, it is not necessary first to combine the two resins.

Table LXXXIX lists formulae for damar-maleic resin combinations. Damar improves gloss and resistance to cold-checking. These varnishes can also be used as vehicles for enamels and architectural whites.

Notwithstanding the drawback of softness and occasional instances of tackiness, damar oil varnishes find a number of applications. Damar films show excellent color stability during baking and bleach upon aging. The collection given in Table XC includes various oils and oil lengths.

[9] U. S. Patent 1,950,417 (1934).
[10] U. S. Patent 1,976,191 (1934).

TABLE LXXXIX

DAMAR-MALEIC RESIN VARNISHES

Formula No.	221		222		223	
Oil length (gal.)	15		25		40	
Composition	lb.	gal.	lb.	gal.	lb.	gal.
Batavia damar A/E	10–40		10		20–40	
Maleic anhydride resin	90–60		90		80–60	
China wood oil	94	12	157	20	157	20
Linseed oil (kettle-bodied—"B" viscosity)	24	3	140	5	161	20
Mineral spirits (150–210°C.)	176	27	240	37	240	37
Toluol	43.5	6	58	8	58	8
Driers—as metal based on oil content						
Per cent lead	0.5		0.5		0.5	
Per cent cobalt	0.02		0.02		0.02	
Preparation of varnish						
Oil added	12 gal. C.W.O.		20 gal. C.W.O.		20 gal. C.W.O.	
Resin and oil heated to	560°F.		560°F.		560°F.	
Held for body	If necessary		If necessary		If necessary	
Check with	3 gal. linseed oil		5 gal. linseed oil		20 gal. linseed oil	
Cool to	400°F.		400°F.		400°F.	
Thin with	Mineral spirits and toluol		Mineral spirits and toluol		Mineral spirits and toluol	
Order of drier addition	After thinner		After thinner		After thinner	

The softness of damar is an advantage in non-skid varnishes (as on a gymnasium floor), or where a flexible film is necessary for the coating of such materials as paper, fabrics, leather, wire. The manufacturer may use only a damar varnish, or he may blend a damar varnish with a harder varnish to improve the former's wear resistance.

East India Oil Varnishes. The value of the East India resins in the field of floor varnishes has already been discussed in connection with the New England Club study.

These resins (batu, black east india and pale east india) are also used in furniture and rubbing varnishes, spar varnishes and metal primers.

The possibility of preparing varnishes without first running these resins has been mentioned in the floor varnish section. Batu and, to a lesser extent, black east india require a slightly more severe thermal treatment than do the pale east indias when incorporated in oils without preliminary processing. In the preparation of varnishes using unrun East India resins, the procedure is to heat the resin along with a portion of the oil, add the remaining oil, and cook to the desired body.

TABLE XC.

Formula No.	224		225		226		227		228	
Oil length (gal.)	5		5		5		5		10	
Composition	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.
Batavia damar	100		100		100		100		100	
China wood oil	39	5								
Linseed oil (kettle-bodied—"B" viscosity)			40	5						
Soybean oil (refined)							39	5	78	10
Perilla oil (alkali-refined)						5				
Mineral spirits (150–210°C.)	98	15	98	15	98	15	98	15	176	27
Toluol	80	11	80	11	80	11	80	11		
Driers—as metal based on oil content										
Per cent lead	0.5		0.5		0.5		0.5		1.0	
Per cent cobalt	0.03		0.03		0.03		0.03		0.06	
Per cent manganese									0.01	
Method of preparation										
Running procedure	None		None		None		None		None	
Preparation of varnish										
Oil added	5 gal. C.W.O.		5 gal. linseed oil		5 gal. perilla oil		5 gal. soybean oil		10 gal. soybean oil	
Preheating temperature	400°F.		400°F.		400°F.		400°F.		400°F.	
Resin added by gently sifting into the oil	100 lb.		100 lb.		100 lb.		100 lb.		100 lb.	
Resin and oil heated to	540°F.		500°F.		500°F.		500°F.		500°F.	
Cool to	300°F.		300°F.		300°F.		300°F.		400°F.	
Thin with	Toluol and mineral spirits		Toluol and mineral spirits		Toluol and mineral spirits		Toluol and mineral spirits		27 gal. mineral spirits	
Order of drier addition	After thinner		After thinner						After thinner	
Properties										
Drying time—tack free	2 hrs.		7 hrs. (soft film)		7 hrs.		7 hrs. (soft film)		6–8 hrs. (soft film)	
Clarity	Clear		Clear		Slightly cloudy		Cloudy		Cloudy	

About 5 gal. of oil should be used with each 100 lb. of resin. This mixture is brought up to 600°F. in about 1 hour. For the pale East India resins, the temperature is then permitted to drop to 540°F. With batu and black east india, however, it is necessary to hold at 600°F. for about 15 minutes before cooling to 540°F. At 540°F. the remainder of oil is added (save for any checking oil) and the whole carried to 560°F. in 20 to 30 minutes. The time at 560°F. will depend upon the oil used and the body desired. The addition of checking oil, thinner, and driers follows normal varnish-making procedure.

Various east india varnishes are to be found throughout this chapter. A number of additional varnishes are given in Table XCI.

Kauri Oil Varnishes. Kauri was the favorite of the old-time varnish maker because of the high quality of the finish and the ease with which the resin could be run. Kauri varnishes, like congo, show a depth

DAMAR OIL VARNISHES

229		230		231		232		233		234		235		236	
10		10		10		25		25		40		40		55	
lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.
100		100		100		100		100		100		100		100	
		78	10					196	25			314	40	432	55
				80	10	201	25			322	40				
78	10														
89	13.7	130	20	156	24	214	33	201	31	280	43	268	41.3	357	55
73	10	36.5	5			172	23.7	160	22	246	34	242	33.3	302	41.7
1.0		0.5		1.0		1.0		0.5		1.0		0.5		0.5	
0.06		0.03		0.06		0.06		0.01		0.06		0.02		0.02	
0.01				0.01		0.01				0.01					
None		None		None		None		None		None		None		None	
10 gal.		10 gal.		10 gal.		25 gal.		25 gal.		40 gal.		40 gal.		55 gal.	
soybean oil		C.W.O.		linseed oil		linseed oil		C.W.O.		linseed oil		C.W.O.		C.W.O.	
400°F.		400°F.		400°F.		400°F.		400°F.		400°F.		400°F.		400°F.	
100 lb.		100 lb.		100 lb.		100 lb.		100 lb.		100 lb.		100 lb.		100 lb.	
500°F.		540°F.		500°F.		500°F.		540°F.		500°F.		540°F.		540°F.	
300°F.		300°F.		400°F.		300°F.		300°F.		300°F.		300°F.		300°F.	
Toluol and		Toluol and		Toluol and		Toluol and		Toluol and		Toluol and		Toluol and		Toluol and	
mineral spirits		mineral spirits		mineral spirits		mineral spirits		mineral spirits		mineral spirits		mineral spirits		mineral spirits	
After thinner		After thinner		After thinner		After thinner		After thinner		After thinner		After thinner		After thinner	
10 hrs.		2 hrs.		5 hrs.		10 hrs.		4 hrs.		24 hrs.		4 hrs.		4 hrs.	
(soft film)				(soft film)		(soft film)				(soft film)					
		Cloudy		Very cloudy		Very cloudy		Clear		Very cloudy		Clear		Slightly cloudy	

of gloss which is greatly desired as well as greater adhesion, particularly to metal surfaces. Formulae are given in Table XCI.

Dehydrated Castor Oil Varnishes. A number of 25-gallon congo varnishes were prepared using various ratios of China wood oil and dehydrated castor oil. The properties of these experimental varnishes along with their method of preparation are given in Table XCII.

Varnishes containing only dehydrated castor oil and the dehydrated castor oil-China wood oil mixtures dried in the same manner as that containing only China wood oil. The dehydrated castor oil varnish dried as rapidly as the others and to about the same hardness. All had good gloss.

In connection with the water resistance of these varnishes, Nos. 246, 247, and 248 showed only slight whitening after 96 hours in tap water, whereas those containing higher percentages of China wood oil showed

TABLE XCI.

East

Formula No.	237		238	
Oil length (gal.)	20		20	
Composition	lb.	gal.	lb.	gal.
Black east india bold scraped	100			
Pale east india			100	
Thermally processed kauri				
China wood oil			126	16
Linseed oil	156	20		
Linseed oil (kettle-bodied—"B" viscosity)			32	4
Linseed oil (kettle-bodied—"R-S" viscosity)				
Mineral spirits (150–210°C.)	240	36.7	260	40
Driers—as metal based on oil content				
Per cent lead	0.8		0.5	
Per cent cobalt	0.02		0.02	
Per cent manganese	0.06		0.01	
Method of preparation				
Running procedure				
Closed (C) or open (O) kettle	(O)			
Temperature (first stage)	600°F.			
Heating time				
Temperature maintained	Until foaming ceases			
Condition of melt				
Temperature (second stage)				
Temperature maintained				
Preparation of varnish				
Oil added			8 gal. C.W.O.	
Preheating temperature				
Resin oil brought to			580°F.	
Heating time			$1\frac{1}{4}$ hrs.	
Temperature maintained			Until oil soluble	
Oil added	20 gal. linseed oil		8 gal. C.W.O.	
Preheating temperature	400°F.			
Resin and oil heated to	600°F.		560–570°F.	
Held for body	To desired viscosity		To desired viscosity	
Check with			4 gal. linseed oil	
Cool to	400°F.		400°F.	
Thin with	36.7 gal. mineral spirits		40 gal. mineral spirits	
Order of drier addition	After thinner		After thinner	
Properties				
Drying time—dust free				
—tack free	8 hrs.		4 hrs.	
Color (Gardner)				
Viscosity (Gardner-Holdt)				
Gloss				
Resistance to cold water				
Additional uses				

Oil Varnishes

India		Kauri					
239		240		241		242	
25		8		25		35	
lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.
100							
		100		100		100	
157	20	63	8	157	20	236	30
				40	5	40	5
40	5						
300	46	160	25	291	45.5	368	57.5
0.4		0.5		0.5		0.5	
0.01		0.02		0.02		0.02	
0.03							
(C)		(O)		(O)		(O)	
610°F.		600°F.		600°F.		600°F.	
1 hr.		1-1¼ hrs.		1-1¼ hrs.		1-1¼ hrs.	
Remove from fire until temp. = 480°F.		½-1 hr. Until foaming ceases		½-1 hr. Until foaming ceases		½-1 hr. Until foaming ceases	
		Oil soluble		Oil soluble		Oil soluble	
625°F.							
1 hr.							
Remove cover							
20 gal. C.W.O.							
400°F.							
560°F.							
5 gal. linseed oil		8 gal. C.W.O.		20 gal. C.W.O.		30 gal. C.W.O	
518°F.		580°F.		560°F.		540°F.	
To desired viscosity		To desired viscosity		To desired viscosity		To desired viscosity	
				5 gal. linseed oil		5 gal. linseed oil	
450°F.		400°F.		400°F.		400°F.	
46 gal. mineral spirits		25 gal. mineral spirits		45.5 gal. mineral spirits		57.5 gal. mineral spirits	
After thinner		After thinner		After thinner		After thinner	
1 hr.							
4 hrs.		1 hr.		4-6 hrs.		6-8 hrs.	
18+							
G							
Good							
Good							
		Rubbing varnish		Floor varnish		Spar varnish	

TABLE XCII

Congo-Dehydrated Castor Oil Varnishes

Formula No.	243		244		245		246		247		248	
Oil length (gal.)	25		25		25		25		25		25	
Composition	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.
Thermally processed congo	100		100		100		100		100		100	
China wood oil	195	25	156	20	117	15	78	10	39	5		
Dehydrated castor oil ("H" to "J" viscosity)			39	5	78	10	117	15	156	20	195	25
Mineral spirits (150–210°F.)	295	45.4	295	45.4	295	45.4	295	45.4	295	45.4	295	45.4
Driers—as metal based on oil content												
Per cent lead	0.5		0.5		0.5		0.5		0.5		0.5	
Per cent cobalt	0.02		0.02		0.02		0.02		0.02		0.02	
Per cent manganese	0.01		0.01		0.01		0.01		0.01		0.01	
Oil added	C.W.O.		C.W.O. and D.C.O.		C.W.O. and D.C.O.		C.W.O. and D.C.O.		C.W.O. and D.C.O.		D.C.O.	
Resin and oil heated to	560°F.		560°F.		560°F.		560°F.		560°F.		560°F.	
Heating time	1 nr.		1 hr.		1 hr.		1 hr.		1 hr.		1 hr.	
Held for body	To desired viscosity		To desired viscosity		15 min.		30 min.		50 min.		60 min.	
Cool to	425°F.		425°F.		425°F.		425°F.		425°F.		425°F.	
Thin with	45.4 gal. mineral spirits		45.4 gal. mineral spirits		45.4 gal. mineral spirits		45.4 gal. mineral spirits		45.4 gal. mineral spirits		45.4 gal. mineral spirits	
Order of drier addition	After thinner		After thinner		After thinner							
Remarks												
Properties												
Drying time—touch	1½–2 hrs.		1½–2 hrs.		1½–2 hrs.		1½–2 hrs.		1½–2 hrs.		1½–2 hrs.	
—hard	4–5 hrs.		4–5 hrs.		4–5 hrs.		4–5 hrs.		4–5 hrs.		4–5 hrs.	
Viscosity (Gardner-Holdt)	J		F		F		D		D		B	
Resistance to cold water	96 hrs.—OK		96 hrs.—OK		96 hrs.—OK		96 hrs.—v. sl. whitening		96 hrs.—v. sl. whitening		96 hrs.—v. sl. whitening	

no whitening. Where whitening was visible, this disappeared within 15 minutes after the panel dried. All the varnishes were somewhat softened.

Dehydrated castor oil and China wood oil differ in rate of bodying. In the mixtures of the two oils, their varnishes were held at top heat for varying lengths of time. Those containing the higher amounts of China wood oil bodied to a higher viscosity and in less time than those containing large amounts of dehydrated castor oil.

Dehydrated castor oil may be satisfactorily used with run congo. Although not a direct substitute for China wood oil, dehydrated castor oil may replace a considerable amount of this oil in a formula with a corresponding longer cooking schedule.

General Utility Varnishes. General utility varnishes are usually medium length varnishes manufactured principally for the "shelf" trade. The consumer regards the varnish as being equally suitable for floors, furniture, boats, inside woodwork, and outside woodwork. The oil length is usually 25 to 35 gallons.

Natural-Synthetic Resin Oil Varnishes. As the specific properties of individual resins were appreciated, combinations were made to obtain mixtures possessing the good qualities of the individual components. Alkyds are blended with damar to improve their gloss and color stability; East India resins are combined with other naturals or with synthetics to secure varying degrees of flatness; a natural may be added to modified phenolics to improve durability as well as the character of their weathering; damar can be used in combination with naturals or synthetics to obtain a desired flexibility; concentrated phenolics are added to natural resins to impart gas-proofness; phenolic and maleic resins may be added to damar to increase its hardness, etc. The formulae in Table XCIII illustrate these blends.

Fifteen-, 25- and 50-gallon varnishes made from blends of natural resins with 25 per cent of 100 per cent phenolic resins proved to be gas-proof, dried rapidly, and had excellent gloss, hardness, adhesion, and weather resistance.

The blended varnishes were prepared by running the resin in the usual manner and adding the preheated China wood oil and synthetic resin. After holding for body, the varnish was checked with linseed oil. Driers were added after centrifuging.

All varnishes were 85 per cent China wood oil and 15 per cent linseed oil. For comparison, blends of naturals with modified phenolics and ester gum were also prepared.

Weathering tests demonstrated the relative values of natural resins

TABLE XCIII.

Formula No.	249		250	
Oil length (gal.)	25		10	
Composition	lb.	gal.	lb.	gal.
Congo No. 11	90			
Thermally processed kauri, congo, or pontianak			80	
Philippine manila bold pale				
Heat-reactive phenolic resin	10		20	
100 per cent phenolic resin				
Modified-phenolic resin				
Cumar				
China wood oil	157	20	78.5	10
Linseed oil	39	5		
Linseed oil (Kettle-bodied—"U-V" viscosity)				
Mineral spirits (150–210°C.)	292	45	208	32
Toluol				
Hi-flash naphtha (150–185°C.)				
Litharge				
Driers—as metal based on oil content				
Per cent lead	0.5		0.5	
Per cent cobalt	0.01		0.02	
Per cent manganese	0.01			
Method of preparation				
Running procedure	Congo		Congo+5 gal. C.W.O.	
Closed (C) or open (O) kettle	(C)		(C)	
Temperature (first stage)	600°F.		400°F.	
Heating time	1 hr.		20 min.	
Temperature maintained	Until foam subsides		Add phenolic—hold 20 min.	
Condition of melt				
Temperature (second stage)	650°F.		560°F.	
Temperature maintained	Until foam subsides		10 min.	
Condition of melt	Oil soluble			
Temperature (third stage)	400°F. Add phenolic and stir			
Preparation of varnish				
Oil added				
Preheating temperature				
Resin and oil brought to				
Heating time				
Oil added	20 gal. C.W.O.		5 gal. C.W.O.	
Preheating temperature				
Resin and oil heated to	560°F.		465°F.	
Held for body	To desired viscosity		20 min.	
Check with	5 gal. linseed oil			
Cool to	400°F.		400°F.	
Thin with	45 gal. mineral spirits		32 gal. mineral spirits	
Order of drier addition	After thinner		After thinner	
Properties				
Drying time—tack free	4 hrs.			
Gloss				
Gas-proofness				

NATURAL-SYNTHETIC RESIN VARNISHES

251		252		253		254	
25		10		25		32	
lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.
		75		50		50	
90							
10							
		25					
				50			
						50	
157	20	60.5	7.7	169	21.5	212	27
39	5			27	3.5	39	5
		18.4	2.3				
292	45	108.5	16.7	300	46.25	260	40
		108	14.9				
						71.6	10
						1	
0.5		0.4		0.4			
0.01		0.0088		0.0088		(0.06 lb.)	
0.01		0.03		0.03		(0.12 lb.)	
Manila		Congo		Congo		Congo	
(C)		(O)		(O)		(O)	
650°F.		650°F.		650°F.		675°F.	
1 hr.		1 hr.		1 hr.			
		1 hr.		1 hr.		Until oil soluble	
		Oil soluble		Oil soluble			
400°F. add phenolic							
Until foaming ceases							
						C.W.O.+linseed+PbO	
						300°F.	
						565–575°F.	
						With stirring	
20 gal. C.W.O.		7.7 gal. C.W.O. then		21.5 gal. C.W.O. then		Add cumar	
		400°F. phenolic		400°F. phenolic			
560°F.		450°F.		560°F.		500–525°F.	
To desired viscosity		To desired viscosity		To desired viscosity		To desired viscosity	
5 gal. linseed oil		2.3 gal. linseed oil		3.5 gal. linseed oil			
400°F.		400°F.		450°F.		400°F.	
45 gal. mineral spirits		Mineral spirits and toluol		46.25 gal. mineral spirits		Mineral spirits and naphtha	
After thinner		After thinner		After thinner		After thinner	
		4 hrs.		4–6 hrs.		4–6 hrs.	
		Excellent				Excellent	
		OK					

and ester gum as modifying or diluting agents for concentrated phenolic resins. In the tests, ester gum showed its characteristic failure by the formation of wide, deep cracks which permitted the elements to undermine the films. This tendency was greater than even 50 per cent of concentrated phenolics could overcome. Modification by naturals repeated the results found previously in natural resin varnishes, i.e.,

Courtesy International Nickel Company, Inc.

FIG. 56. Kettles over heaters in varnish stacks. Kettles are of Monel metal, 250 gallons, 46 inches in diameter, and 36 inches in depth. Sides are ⅛ inch thick and bottom is 3/16 inch.

their more satisfactory weathering characteristics were shown by freedom from premature cracking and the gradual and uniform wearing of the panel over its entire area.

Fritz[11] reviewed attempts to prepare varnishes from copals without running them. Krumbhaar[12] described the esterification of rosin and other natural resins as well as the compatibility with oils, solvents, and pigments. Hornemann[13] detailed the German viewpoint on damar

[11] F. Fritz, *Farbe u. Lack*, 1936, p. 573.

[12] W. Krumbhaar, *Official Digest*, Fed. Paint, Varnish Production Clubs, No. 139, 259-69 (1934).

[13] C. Hornemann, *Farbe u. Lack*, 1933, pp. 43-4.

and its uses. Nolte[14] indicated that dampness was a predominating cause along with thick films for bloom on varnish coatings. Congo and pontianak copal varnishes were free from this difficulty when the varnishes were properly prepared, although tung oil has a bloom-producing tendency. Arnold and Frost[15] in a study of the methods of testing of insulating varnishes showed that the wire enamels in general were China wood oil-fossil resin materials. Krauz and Fischmann[16] state that every type of resin requires a specific variety of drier whose quantity is important. This resulted from their study of driers in a wide range of natural resin varnishes. Harrison and Fonrobert[17] directed attention to the bloom of varnishes, indicating that driers, free resin, or fatty acids, thinners, badly cooked oils, badly cooked run gum, free glycerin, and film thickness were contributing factors. They recommended specific formulations for non-blooming varnishes. Krauz and Krach[18] studied damar varnishes with oils such as linseed, hempseed, locust seed, soybean, poppyseed, and walnut, and the effect of specific driers, particularly different forms of metallic oxides, on the properties of these varnishes. Wolff and Zeidler[19] compared short and long oil varnishes from kauri and congo with the various Albertols and indicated that the copals were the equals of the Albertols. Scheiber[20] showed that the acid value of a resin is no criterion of its ability to displace fatty acids during the cooking of the varnishes. They indicated that a high acid value natural resin need not necessarily produce a varnish with free fatty acids.

[14] H. Nolte, *Farbe u. Lack,* 1932, pp. 413-4, 425-6, 439-40.

[15] R. H. Arnold and L. E. Frost, *Elec. Mfg.,* **10,** No. 4, 39-40 (1932).

[16] C. Krauz and F. Fischmann, *Chem. Obzor,* **6,** 257-60, 289-90, 309-18 (1931); *Chem. News,* **144,** 161-3 (1932).

[17] A. W. C. Harrison and E. Fonrobert, *Farben-Ztg.,* **36,** 1467-9, 1512-4, 1554-6, 1601-3, 1645-6 (1931).

[18] *Chem. News,* **137,** 257-60 (1928).

[19] H. Wolff and G. Zeidler, *Farben-Ztg.,* **34,** 2458-9 (1929).

[20] J. Scheiber, *Farbe u. Lack,* 1929, pp. 393-4, 404-5, 418-9.

CHAPTER XIX

SPIRIT VARNISHES

A spirit varnish is essentially a resin solution which dries by evaporation of solvent with or without the application of heat. It may vary from a simple solution of a resin in a single solvent to a complex mixture of several resins in a mixed solvent modified with any of a number of non-resinous materials excluding those solutions which contain cellulose derivatives.

Spirit varnishes are less durable than drying oil varnishes. They are easy and inexpensive to prepare and apply. Since they produce brilliant and transparent finishes, they find extensive use in applications in which durability is of secondary importance.

The natural resins are soluble in a large variety of solvents and form transparent films having good adherence. Since the mechanics of resin solvation have become better understood and basic information on natural resin solvents more readily available, many formulative difficulties and inconsistencies have been eliminated.

Spirit varnishes are formulated to fulfil a wide variety of requirements and to produce films from a dull or "mat" finish through the varying degrees of semi-gloss to finishes of exceedingly high luster. The varnish film may be transparent, semi-transparent or opaque and, if desired, colored by inclusion of soluble dyestuffs or insoluble pigments.

Spirit varnishes need less drying time than that required by oil varnishes. Upon evaporation of the solvent, the film formed contains no constituent which dries by oxidation and, therefore, retains unaltered many of the characteristics inherent in the resin. The simplicity of preparation of spirit varnishes has all too often led to thoughtless formulation and total disregard for such factors as relative hardness, solvent retention, rate of solvent evaporation, viscosity, and thickness of film applied.

In general, the gloss increases with the hardness of the resin. Thus, a hard manila will give higher gloss than a soft manila and a hard damar more than a softer damar. The damars yield higher gloss than the harder Manila copals.

Hardness and high luster of resins are seldom accompanied by elas-

ticity and toughness. Thus, a simple spirit varnish consisting of a hard resin dissolved in a single solvent may form a hard, bright, and lustrous but brittle film, while a softer resin may produce a less lustrous film with a greater degree of flexibility. The film will, however, decrease in flexibility with age, although the duration of the flexibility may far exceed the expected life of the varnish film.

The film flexibility obtained from a spirit varnish is dependent upon the hardness and solvent-retention properties of the resin and upon the volatility of the solvent. The hardness of a natural resin is also a measure of its content of essential oil. In the softer resins these oils are present in sufficient quantity to plasticize the resin film effectively and thus render it flexible. The essential oils are subject to volatilization and, although the rate of such volatilization may be small, it is accelerated when the resin is exposed in thin varnish films. There is also a gradual release of the solvent retained by the resin irrespective of the resin's solvent-retention properties, although the magnitude of such properties and the volatility of the solvent do determine to a large extent the rate of such solvent release.

For many of the applications of spirit varnishes, such as certain types of paper coating, gloss coatings for hard candies, and finishes for children's toys, the anticipated life of the finish is short. Proper selection of the resin with respect to solvent retention and of the solvent with respect to evaporation rate will provide a satisfactory varnish, inasmuch as the loss of flexibility proceeds very slowly. In still other cases a longer life or much higher degree of flexibility may be required. The desired results may then be obtained by the inclusion of a plasticizer.

In order to appreciate the importance of such factors as the choice of solvent, solvent retention, rate of solvent evaporation, viscosity, and the effect of mixed solvents upon spirit varnish formulation, it is necessary that a basic knowledge of resin solvation be acquired. Resin solutions are not comparable to solutions of salts in water, since they do not possess a saturation point and since between resin and solvent there exists the phenomenon of mutual solubility. Resin solubility postulates the presence of active groups upon the resin and solvent molecules, between which groups an attractive force exists. Solubility results when the existing force is of sufficient magnitude to overcome the forces of cohesion. At low concentrations it is probable that the resin is dissociated into individual resin molecules and represents a true solution. At higher concentrations the resin may exist as aggregates of colloidal dimensions. At still higher concentrations the aggre-

gates become sufficiently large to cause formation of a gel structure which may be broken down by violent agitation but which will re-form upon standing.

In every resin solution there then exists an equilibrium between the tendency to solvate and the tendency to aggregate. Changes in concentration upset this equilibrium, causing a change in the size of the resin aggregates and a corresponding change in the viscosity of the solution. Substitution of a second solvent, whether a solvent of different strength or a diluent, for a portion of the original solvent would disturb the equilibrium in the solution. A new equilibrium would then be established in which the size of the resin aggregates would be altered, and a corresponding decrease or increase in viscosity would occur depending upon whether the substituted solvent was a stronger or weaker solvent for the resin than the original solvent. Addition of sufficient diluent would eventually result in gel formation. Should the change in solvent composition be made to take place rapidly, i.e., a rapid addition of diluent, without allowing sufficient time for the establishing of equilibrium conditions with each successive change, a point would be reached at which the existing degree of solvation would no longer be sufficient to maintain the aggregates in solution. Precipitation of the resin would occur. A similar occurrence would take place with rapid changes in concentration, i.e., a rapid dilution with the same solvent or another solvent. Thus, a solution of Manila copal in alcohol will precipitate a portion of the resin upon rapid dilution with more alcohol. A similar action will also take place with damar in petroleum solvents.

Similar changes occur within the varnish film during its drying period. The solvent, therefore, has a direct influence upon the nature of the film produced and by proper selection of solvent combinations it is possible to obtain markedly different finishes with the same resin. By selecting a very volatile solvent, the concentration changes in the drying film can be made to take place with sufficient rapidity to produce a partial precipitation of the resin and thus cause formation of a dull or "mat" finish which is likely to be translucent. On the other hand, the same resin, when used with a solvent of lower evaporation rate which permits sufficient time for the establishment of equilibrium conditions during the drying period, can be made to yield a transparent film of high luster. An example is found in one method for producing sandarac mat finishes wherein the solvent is largely composed of ethyl ether.

Formula 255

2½ lb. sandarac
½ lb. mastic
17¾ lb. (3 gal.) ethyl ether

then add a mixture of

4½ lb. (¾ gal.) ethyl ether
3¾ lb. (⅝ gal.) benzine

Similar effects are of more importance in spirit varnishes in which mixed solvents are employed. In addition to the effects of increasing resin concentration during the evaporation of the solvent, the concentration ratios of the solvent components are continually changing unless the evaporation rates of such components are approximately equal. In a system in which the diluent possesses a lower evaporation rate than the solvent, it is possible that a sufficient concentration of diluent may be attained during the drying of the film to cause gelation or partial precipitation of the resin. Such considerations have effects upon the gloss, hardness, adhesion, and durability of the varnish film.

The solvent and diluent control the viscosity of the resulting spirit varnish at any given resin concentration and thus, indirectly, the film thickness. The consistency of a spirit varnish should be regulated according to the volatility of its solvent; the more volatile the solvent, the less viscous should be the varnish. In the film of a viscous spirit varnish containing a volatile solvent, drying occurs at the exposed surface with great rapidity. The skin formed by this rapid drying impedes the escape of solvent from the remaining varnish beneath the surface and causes an abnormal retention of solvent. The varnish beneath the surface is then subject to repeated softening and hardening with relatively slight changes in temperature, causing wrinkles and other defects.

A variety of methods are open to the formulator for the alleviation of this condition. (1) The concentration of resin may be altered. (2) Some other solvent of equivalent volatility but producing a lower viscosity may be employed. (3) A less volatile solvent which will permit use of the same viscosity but provide uniform drying throughout the film may be selected. (4) A small amount of a stronger resin solvent may be substituted in or added to the original varnish to reduce its viscosity without appreciably affecting its volatility. The latter is a common method for reducing the viscosity of resin solutions. For example, a viscous solution of damar in turpentine can be

rendered quite fluid by the addition of a small amount of toluol. Likewise, a resin solution of low viscosity may be rendered more viscous by the addition or substitution of an appropriate non-solvent in the formulation. The changes in viscosity vary with the choice of solvents and the resin concentration, the more rapid changes taking place in the higher ranges of viscosity.

It is not always possible to draw definite conclusions as to solubility in mixed solvent systems from the solubility data for the individual solvents. Formulative possibilities exist which are unpredictable. Little authentic information as to solvation tendencies for binary and multiple solvent systems is now available.

Combinations frequently neutralize undesirable properties existing in one or both resins and produce a varnish which cannot be equaled by either of the individual resins. An example is found in the simultaneous use of damar and Manila copals in a solvent comprised of approximately equal proportions of a hydrocarbon solvent and an alcohol. The damar serves as a plasticizer for the manila and also improves the adherence, while the manila acts as a hardening component, producing a harder and more durable film than would be obtained with damar alone.

The preparation of spirit varnishes is simple. The resin and solvent are agitated together either in the cold or with application of heat. Solution is more rapidly obtained at elevated temperatures and the resulting varnish will possess a more brilliant luster. Such solutions may be darker in color and may not possess as good adhesion as those obtained by cold cutting. The solution is clarified by sedimentation, filtration, or centrifuging.

Where mixed solvents are to be used, two methods of solution are possible. The resin may be dissolved in the solvent and the diluent added after solution is complete, or the resin may be dissolved directly in the mixed solvent. Industrially the latter method is usually preferable. The introduction of a diluent, even when added slowly and with agitation to permit the necessary equilibrium changes, results in a momentary localized concentration of diluent at the point of introduction. Some precipitation may occur, but usually it is negligible, with re-solution occurring almost instantaneously. With certain solvent combinations re-solution takes place more slowly and a cloudy solution results which is difficult to clarify.

The bulk of spirit-varnish consumption has centered about relatively few industries, such as paper coatings, furniture finishes, leather finishes, sanding sealers, and shellac substitutes. The spirit varnishes

for these purposes are subject to frequent modification according to the conditions of use and the fluctuations in the market value of the raw materials. The information on formulations is small in comparison with the volume of spirit varnishes consumed annually.

The resins most widely used are the manilas and the damars. Batu and the east indias find applications where color is a secondary consideration. Mastic and sandarac are spirit-varnish resins but their cost limits their applications. Elemi alone is too soft, but is a plasticizer for spirit varnishes and adhesives. Damar is light in color, yields films of a high gloss and good adhesion, and shows no tendency to yellow on standing but bleaches to colorless films when exposed to sunlight. It is a soft resin and has a high solvent retention and is, therefore, self-plasticizing to a large extent. Damar has a tendency to soften at elevated temperatures. The resin possesses a high solvent retention so that superficial drying may occur if thick films are laid down, or the varnish is poorly formulated.

Damar spirit varnishes are, in general, paler, more lustrous, more flexible, and show better adherence than those obtained from manila solutions. Damar is essentially a resin for indoor purposes.

For clear wall varnishes and interior enamels not subjected to handling or abrasive wear, damar solutions in turpentine or hydrocarbon solvents are applied to ceilings and the upper portions of walls. Where the coating is subjected to moderate temperatures, damar spirit varnishes and enamels offer a freedom from yellowing difficult to attain with other resins. The resulting finishes possess high gloss and a high degree of fume-proofness.

Damar has been used both alone and in conjunction with other resins in the production of photographic finishes. An interesting use is to be found in a method[1] for making reproductions of fingerprints. The latent fingerprint is exposed to iodine vapors and then covered with a sheet of slightly moistened paper containing a paste of rice starch and potassium iodide. The image is varnished with a dilute (3 per cent) solution of damar in benzene. It is claimed that a bluish brown print is obtained and that several replicas can be made. Damar solutions, by virtue of their non-reactive and non-yellowing properties, are vehicles in luminous paints.

The major portion of damar spirit varnishes are utilized in formulations containing other film-forming constituents which compensate for the softness inherent in damar films. The most extensive use of damar spirit varnishes as addition agents is in the field of cellulosic lacquers

[1] M. Wagenaar, *Pharm. Weekblad,* **72,** 1265-71 (1935).

to which damar imparts the necessary adhesion and gloss as well as maintains the desired light color in the film. They are used as addition agents in alkyd enamels to prevent yellowing during the baking operation (Chapter XXI, p. 409). With chlorinated rubber they are used as paper coatings for many purposes. Damar solutions in benzol are used in the preparation of rubber cement, and damar with other constituents such as elemi and vegetable pitches in a variety of adhesives.

The Manila copals are the most widely used spirit-varnish resins. The films are not quite so pale as those obtained with the corresponding grades of damar, nor do they possess so high a degree of flexibility and adherence. The manilas, however, provide films of good color which are harder and more durable than those of damar and are therefore preferred for many purposes. The tendency toward brittleness of film is overcome by proper plasticizers, which also improve the adhesion.

In general, the manila grades give increasing luster with increasing hardness of the resin. The ease of solubility decreases with increasing hardness. Manila spirit varnishes are extensively used as sanding sealers, a typical example of which follows:

Formula 256

25 lb. manila DBB
55 lb. (8.28 gal.) denatured ethyl alcohol
20 lb. (3.0 gal.) butanol

The properties desirable in a sanding sealer are (1) a relatively hard resin, (2) rapid penetration into the pores of the wood, (3) ease of application whether by brushing or spraying, (4) complete and fairly rapid drying (low solvent retention), and (5) ease of sanding. The resin concentration in sanding sealers is kept low (rarely exceeding 30 per cent), in order to insure rapid penetration into the wood. Manila solutions in which alcohol is the only solvent do not brush easily. The inclusion of butanol in the formulation improves the brushing properties and reduces the evaporation rate sufficiently to permit a greater amount of penetration into the wood. If the sealer is to be applied by a spray gun, it is necessary that a small amount of a high-boiling solvent be included in the formulation to counteract the tendency of the finish to dry with an orange-peel effect.

Since the manilas are alcohol soluble, they are the logical starting point in the preparation of shellac substitutes. The solvents for the manilas also dissolve a variety of dye and coloring matters, making possible highly colored transparent varnishes and aniline inks. Plas-

ticized manila solutions enter the field of paper coating and leather finishes. The formulations vary mainly in the evaporation rate of the solvents, in accordance with the speed of the coating operation. Manila solutions find use in the preparation of enamels, providing that the use of reactive pigments be avoided. Probably the largest single use of manila spirit varnishes is as a vehicle in the production of traffic paints.

Manila solutions are much used as finishing coats for inexpensive furniture and wooden novelties. Alone and with other ingredients, they serve as insulating varnishes and impregnating media for textile fabrics. They enhance the brilliance of costume jewelry and at the same time by protecting the metal surface prevent tarnishing. Concentrated manila solutions are bookbinder's varnish and, with other components, are cements for various purposes.

Batu and the east indias enter the spirit-varnish field mainly in the production of sanding sealers and chemically resistant and mat finishes. They are the most inert and chemically resistant of the natural resins and are used both alone and with such materials as chlorinated rubber in acid and alkali resistant coatings.

Mat finishes are obtained from spirit varnishes in three ways: (1) from a resin yielding films of low gloss, (2) by solvent formulation, and (3) by addition of flatting agents such as aluminum stearate, waxes, chlorinated rubber[2] (Table XCIV), and diatomaceous earth. Usually a combination of these methods is met. Solutions of batu which has not been thermally processed give dull films. Batu is usually the resin chosen for mat finishes where light color is not an important factor. The principal use of such varnishes is for finishing furniture in varying degrees of dullness or semi-gloss.

Because of their insolubility in the usual paint and varnish thinner of petroleum or coal-tar origin, Manila resins find application in the preparation of wood fillers or sealers. The formulae listed in Table XCV also include two pale east india solutions.

Mastic and sandarac spirit varnishes are utilized by artists for the protection of fine paintings and photographs.

Natural Resins in Chlorinated Rubber Coating Compositions. Where surface coatings must resist the action of moisture, acid, alkali, and the like, the coating may be fortified by chlorinated rubber. Solutions of damar, mastic, elemi, run congo, and run damar may be so treated. The east indias show some incompatibility but not sufficient to cause

[2] A. Skett, *Paint, Oil Chem. Rev.*, **102**, 11 (1940).

TABLE XCIV

FLAT SPIRIT VARNISHES

Formula No.	257		258	
	lb.	gal.	lb.	gal.
Batu scraped	80		80	
Chlorinated Rubber—L.V.	2		2	
China wood oil	10	1.27	10	1.27
Refined linseed oil	20	2.56		
Raw soybean oil			30	3.90
Toluol	200	27.7	200	27.7
Gloss	Almost flat		Flat	
Flexibility just after drying	Very good		Very good	
Hardness " " "	Soft		Soft	
Flexibility after 7 hrs.	Very good		Very good	
Hardness " 7 "	Soft		Soft	
Flexibility " 48 "	Fair		Very good	
Hardness " 48 "	Hard		Soft	
Flexibility " 2 weeks	Fair		Good	
Hardness " 2 "	Very hard		Hard	
Remarks	No change due to aging after 2 months		No change due to aging after 2 months	

appreciable reduction in adhesion or durability. The varnishes have a dull finish and show resistance to chemical action.

Solutions of chlorinated rubber with those resins showing complete compatibility have been tested for resistance to 25 per cent sulfuric acid, 5 per cent sodium hydroxide, cold water, gasoline, saturated salt solution, 50 per cent alcohol, and boiling water. The varnishes (Table XCVI) contained 20 per cent solids with chlorinated rubber and resin in the ratios 1 to 2, 1 to 1, and 2 to 1.

Chlorinated rubber-natural resin varnishes are suitable for moisture–vapor-proof coatings for paper. Typical formulations are listed in Table XCVII. Formulations 289 and 290 give very flexible films which are softer than those obtained with formulae 287 and 288.

The inertness of chlorinated rubber to the action of alkalies makes finishes containing that material particularly adapted to use on cement, plaster, brick and similar surfaces. Typical formulations are listed in Table XCVIII. Two coats are recommended, inasmuch as

TABLE XCV

Wood Sealers

Formula No.	259		260		261		262		263		264		265		266		267		268		269		270	
	lb.	gal.	lb.	gal.	lb.	gal.	lb	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.
Loba dust	50	...	50	...	...	...	50	...	...	...	...	...	50	...	50	...	25	...	25	...	...	...	25	...
Pontianak bold scraped	...	...	...	...	...	...	...	...	33	...	33	...	...	...	...	...	...	...	...	...	...	...	...	...
P.E.I. Macassar nubs	...	...	...	...	50	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	25	...	...	...
Butanol	...	...	...	...	...	...	...	...	...	...	...	...	50	7.41	...	...	...	...	...	...	...	...	...	...
Amyl alcohol	...	...	...	...	...	...	...	...	...	...	...	...	...	...	50	7.39	...	...	...	...	...	...	...	...
Cellosolve	50	6.45	...	...	...	...	...	...	67	8.64	...	...	...	...	...	...	...	...	75	9.68	...	...	...	...
Butyl Cellosolve	...	...	50	5.62	...	...	...	...	...	...	67	7.53	...	...	...	...	75	8.42	...	...	...	...	...	...
Carbitol	...	...	...	...	...	...	50	5.85	...	...	...	...	...	...	...	...	...	...	...	...	...	...	75	8.77
Solvesso No. 2	...	...	...	...	50	7.05	...	...	...	...	...	...	...	...	...	...	...	...	...	...	75	10.57	...	...

TABLE XCVI

Resin Solution	Formula No.	Ratio Chlorinated Rubber to Resin	Resistance to						
			25 per cent H_2SO_4	5 per cent NaOH	Cold water	Gasoline	Saturated salt solution	50 per cent alcohol	Boiling water
Batavia damar A/E-chlorinated rubber in Hi-flash naphtha	271	1 : 2	OK—120 hrs.	White film—24 hrs.	OK—120 hrs.	White film—45 min. Failed to adhere—120 hrs.	OK—120 hrs.	OK—120 hrs.	Failed—5 min.
	272	1 : 1	" " "	Failed—120 hrs.	" " "		" " "	" " "	" " "
	273	2 : 1	" " "	OK—120 hrs.	" " "		" " "	" " "	" " "
Thermally processed congo No. 11—chlorinated rubber in Hi-flash naphtha	274	1 : 2	" " "	Failed to adhere—5 hrs.	" " "	White film—45 min. OK—120 hrs.	" " "	Failed to adhere—120 hrs.	Failed—4 min.
	275	1 : 1	" " "	Failed to adhere—5 hrs.	" " "	White film—45 min.	" " "	OK—120 hrs.	" 5 "
	276	2 : 1	" " "	OK—120 hrs.	" " "	Failed to adhere—120 hrs.	" " "	" " "	" " "
Thermally processed congo No. 11—chlorinated rubber in octyl acetate	277	1 : 2	" " "	OK—24 hrs. Failed—120 hrs.	" " "	White film—45 min. OK—120 hrs.	" " "	Failed to adhere—120 hrs.	" " "
	278	1 : 1	" " "	OK—120 hrs.	" " "		" " "	OK—120 hrs.	" " "
	279	2 : 1	" " "	" " "	" " "		" " "	" " "	" " "
Mastic—chlorinated rubber in octyl acetate	280	1 : 2	" " "	White film—24 hrs. Failed—120 hrs.	" " "	White film—45 min. OK—120 hrs.	" " "	" " "	" 2 "
	281	1 : 1	" " "	OK—24 hrs. Failed—120 hrs.	" " "		" " "	" " "	" 4 "
	282	2 : 1	" " "	OK—120 hrs.	" " "		" " "	" " "	" 6 "
Elemi—chlorinated rubber in octyl acetate	283	1 : 2	" " "	OK—24 hrs.	" " "	White film—45 min. Failed to adhere—120 hrs.	" " "	" " "	" 5 "
	284	1 : 1	" " "	Failed—120 hrs.	" " "		" " "	" " "	" " "
	285	2 : 1	" " "	OK—120 hrs.	" " "		" " "	" " "	" " "

TABLE XCVII

PAPER FINISHES

(All weights in pounds)

Formula No.	286	287	288	289	290
Batavia damar A/E	...	10	...	33	18
Thermally processed congo	...	...	10	...	...
Pale east india chips	14	...	...	...	...
Elemi	...	...	...	10	20
Chlorinated rubber (125 cp.)	22	10	10	7	12
Tricresyl phosphate	...	2	2	...	...
Diamyl phthalate	9	...	...	...	...
Hi-flash naphtha	...	78	78	...	...
Toluol	51	...	...	50	50
Paraffin wax (m.p. 60°C.)	4	...	...	...	...
Solids (per cent)	40	50	50	50	50
Moisture-proof	Yes	Yes	Yes	Yes	Yes
Tasteless	Yes	Yes	Yes	Yes	Yes
Odorless	Yes	...	...	...	...
Non-toxic	Yes	Yes	Yes	Yes	Yes

the first acts as a sealing coat. Coatings are little affected by water at 115°F. and show little or no effect after 24-hour immersion tests in cold water, concentrated hydrochloric acid, and sodium hydroxide solutions. The films air-dry in less than 48 hours at ordinary temperature and are hard, durable, and very flexible. When applied to sheet metal of collapsible tubes, satisfactory adhesion is obtained. Although the metals cracked from fatigue in a bending test, no cracking, chipping, or breaking of the film occurred. Formula 291 was unaffected by an immersion test in 95 per cent ethyl alcohol.

East indias with drying oils and smaller percentages of chlorinated rubber have been found desirable in finishing inexpensive furniture and wooden novelties. The films are flexible and tough. Two typical formulations are given in Table XCVIII.

Production of Transparent Papers. Experimental work has indicated that natural resin spirit varnishes have possibilities for transparent paper for window envelopes. Transparency is chiefly a question of penetration into the pores of the treated paper. The ideal combination must dry quickly and completely, leave a smooth, glossy surface, and penetrate the fibers of the paper to a degree which permits one to read any type through it clearly. The material must be adapted to machine

TABLE XCVIII

	Alkali-Resistant Finishes				Furniture Finishes	
Formula No.	291	292	293	294	295	296
Batavia damar	50	...	50	...	...	...
Batu bold scraped	...	...	...	...	25	25
Run congo	...	50	...	50	...	...
Chlorinated rubber	100	100	100	100	1	1
High aromatic petroleum naphtha	350	350	...	...	...	...
Toluol	...	...	350	350	48	64
Hi-flash naphtha	...	...	...	...	16	...
China wood oil	...	...	...	...	...	7
Hydrogenated methyl abietate	30	30	30	30	...	...
Linseed oil	...	...	...	...	10	3

operations involving either dipping, coating by rollers, or coating only small areas as by a printing pad or a roller with a section of its surface depressed. Transparency may be achieved by coating one or both sides of the paper. The viscosity of the coating medium is important. It must be heavy enough for printing press operations, yet retain sufficient flow to provide the smooth finish desired.

The logical resins are the damars, which are petroleum and coal-tar solvent soluble, and the manilas and sandarac, which are alcohol soluble.

Solutions were applied by flowing to both sides of the paper. After drying thoroughly, the papers were examined. The formulations used and the results obtained are tabulated in Table XCIX. The best results were obtained with formulations 300 and 302.

Stock[3] made a compilation of gloss-coating formulations using accroides and spirit-soluble manilas or combinations with artificial resins. Bragdon[4] described coatings employing damar, shellac, and other resins with nitrocellulose for finishing photographs, paintings, color-prints, maps, blueprints, sketches, and drawings on paper or canvas.

[3] E. Stock, *Farben-Chem.*, **9**, 7, 12 (1938).

[4] C. R. Bragdon, *Ind. Finishing*, **10**, No. 2, 11-14 (1933).

TABLE XCIX*

Formula No.	297	298	299	300	301	302
20 per cent Batavia damar A/E —toluol	30	...	...	...	...	...
50 per cent Batavia damar A/E —benzol	...	30	30	30	30	30
Butyl lactate	...	...	...	1	...	...
Drier	...	...	...	...	...	0.10
Linseed oil (5-hr., kettle-bodied)	...	...	...	...	...	1
Mineral seal oil	1	2	...	...	1	...
Octyl acetate	...	2	2	2	2	2
Translucency	Good	Good	Good	Good	Good	Good
Transparency	...	Good	Good	Good	Good	Good
Penetration	...	Good	Good	Good	Good	Good
Gloss film	...	Good	Good	Good	Good	Good
Readability†	...	Good	Good	Good	Good	Good
Tackiness	...	Slight	None	None	None	None

* Figures indicate parts by weight.

† The term readability used in the above table is explained as follows: The sheets of paper with the solutions on them were placed over a typewritten sheet; the sharpness of the type when viewed through the treated papers determines the "readability" which was classed as poor, fair, or good.

CHAPTER XX

LACQUER FORMULATIONS

When the tree *Rhus vernicifera*, known in Japan as Urushi No-ki and in China as Tsichou, is tapped, a natural varnish is obtained. This material is known as urushi natural lacquer and Japanese or Chinese lacquer. Its use was described by D'Incarville in 1760.[1] According to Chinese legend, these lacquers were used as early as 1169 to 255 B.C. and their application reached a high standard of performance in the Ming dynasty, A.D. 1368 to 1644 Quinn,[2] in 1880, Dick,[3] Araki,[4] and Young[5] described the lacquering procedures. Sabin states that the tree yields are 56 to 90 g. of resin when the trees are tapped for seven weeks at intervals of seven days, after which there is a rest period of five to seven years. The tree exudation is a milky liquid which must be stored in closed containers, otherwise darkening and thickening on exposure occurs. The lacquer will not harden in a dry atmosphere, but does so rapidly in the presence of moisture at about 20°C. Its drying was investigated by Hixon and Zee.[6] Yoshida[7] gave the composition as volatile matter and water 9.4 per cent, nitrogenous matter 2.3, gummy constituents 3.15, and a material designated urushic acid 85+ per cent. Urushiol and related materials produce dermatitis as a result of a poisonous ingredient stated by Tschirch and Stephan[8] to be an oily, non-volatile substance soluble in petroleum ether. Livache[9] describes the methods of analysis of raw lacquers of the urushiol type.

Resin solutions in solvents, particularly when the solvent was alco-

[1] C. A. Sabin, *J. Soc. Chem. Ind.*, **29**, 1320 (1910).

[2] *Trans. Asiatic Soc.*, Japan, 1880.

[3] S. Dick, *Bull. Imp. Inst.*, **8**, 32 (1910).

[4] F. S. Araki, *Ind. Finishing*, December, 1928, p. 30; February, 1929, p. 95; January, 1930, p. 44.

[5] C. D. Young, *Ind. Finishing*, December, 1928, p. 30.

[6] A. W. Hixon and Z. Z. Zee, *Paint, Oil and Chem. Rev.*, **81**, No. 15, 10 (1926); No. 16, 10; No. 17, 10; No. 18, 10; No. 19, 10; No. 20, 10.

[7] H. Yoshida, *Trans. Chem. Soc.*, **43**, 472 (1883).

[8] *Arch. Pharm.*, **243**, 504 (1905).

[9] Ach. Livache and J. G. McIntosh, "The Manufacture of Varnishes and Kindred Industries," Vol. III, second edition, pp. 239-59, Scott, Greenwood & Son, London, 1911.

hol or "spirit," were called "spirit varnishes." When nitrocotton, pyroxylin, or celluloid were used, Livache referred to them as collodion or celluloid spirit varnishes. A change in terminology has come about by which the term "lacquer" denotes "spirit varnishes" drying by evaporation, in which a cellulose derivative constitutes a major film-forming ingredient. When pigments are incorporated, the products are referred to as lacquer enamels.

The industrial development of cellulose lacquers was accelerated by the search for uses of large surpluses of nitrocellulose and solvents such as acetone and butanol at the end of the First World War in 1918; by the development of low-viscosity nitrocotton not long afterwards, so that higher solids content with lower-viscosity solutions could be produced, coupled with the demand of the expanding automotive industry for rapidly drying finishes more adaptable to assembly lines than the slow-drying varnishes then employed.

Lacquer technology has developed an extensive literature.[10] Cellulose lacquers are applied in large quantities to almost every type of surface. The formulation, production, and application of cellulose lacquers has become a highly specialized field.

Lacquers usually consist of five components: a cellulose derivative, one or more resins, a plasticizer, a solvent, and a diluent. Of these components the latter two are collectively termed the "lacquer solvent" whereas the remainder constitute the solids content. The solvent and the diluent may be, and usually are, complex mixtures rather than single component systems.

Inclusion of resinous materials in nitrocellulose lacquers dates from about the year 1885. Practically all the cellulosic lacquers contain resin. The property of film adhesion, lacking in a pure cellulosic film, is imparted to metal, glass, and other smooth surfaces by resins. The resin does not perceptibly affect the viscosity of the solution. Lacquers may then have a higher solids content than can be obtained with a cellulose derivative alone. Resins are usually less expensive than the cellulose derivatives, and enhance the gloss of the finish, particularly in enamels.

Plasticizers are used in lacquers to impart flexibility to the dried film and should be mutual solvents for the cellulose derivative and the resin. The resin must be compatible with the cellulose derivative, and

[10] S. P. Wilson, "Pyroxylin Enamels and Lacquers," D. Van Nostrand Company, 1927; B. K. Brown and F. M. Crawford, "A Survey of Nitrocellulose Lacquer," The Chemical Catalog Company, 1928; A. Jones, "Cellulose Lacquers, Finishes and Cements," J. B. Lippincott Company, 1938.

the plasticizer must be compatible with both of them. Reference should be made to the compatibility tables at various points in this volume.

A complicating factor in lacquer formulation is the difference between the solubility of nitrocellulose and resins. Nitrocellulose is most readily soluble in esters, ethers, ketones, keto-alcohols and the hydroxy-esters, while the resins are more soluble in alcohols and hydrocarbon solvents.

Nitrocellulose solvents and diluents are customarily referred to as either "high" or "low" boilers, with the dividing point the boiling point of water. The volatility of any solvent or diluent is dependent upon its vapor pressure at the temperature of evaporation rather than at the boiling point. The selection of lacquer solvents and diluents is based upon relative rates of evaporation together with such influencing factors as molecular weight and latent heat of vaporization. The presence of the cellulose derivative and the resin usually has a direct effect upon the speed of evaporation of the lacquer solvent.

A difficulty encountered in the formulation of cellulose lacquers is "blushing." Three types may occur, namely, water blushing, cotton blushing, and "gum" or resin blushing. The last two are often evidence of incompatibility. The occurrence of a blush upon a lacquer film may be temporary, i.e., the film may blush during the process of drying, but the blush disappears before the film is completely dry. The blush may be permanent and result in non-adherent, poor films of low tensile strength.

A frequent cause of blushing in lacquer films is water. If the evaporation of the volatile components of the lacquer solvent is sufficiently rapid to lower the temperature of the air surrounding the lacquer film below the dew point, moisture condenses upon the film. The condition is corrected by the inclusion of additional high boilers to lower the evaporation rate and thus reduce the cooling effect. Since water blushing is a function of both temperature and humidity, occasionally a lacquer, free from blushing under normal conditions, will show a distinct water blush if the weather is hot and humid. Temporary blush is corrected by changing the solvent balance, that is, the ratio of high to low boilers.

Cellulose derivatives show no solubility limits other than those dictated by viscosity. The solutions, as for resins, are colloidal in nature. A lacquer comprising both of these systems is in easily disturbed colloidal balance. This balance must be maintained during the drying period, in which the ratio of volatile to non-volatile, as well as

the ratio of the individual volatile components to each other, is continually changing.

The graphical methods described by Hofmann and Reid[11] depict the relationship between the resin and other lacquer ingredients as well as the methods of controlling the various properties of the final film. In this method, a lacquer is considered to consist of two portions: the non-volatile portion and the volatile portion. The non-volatile

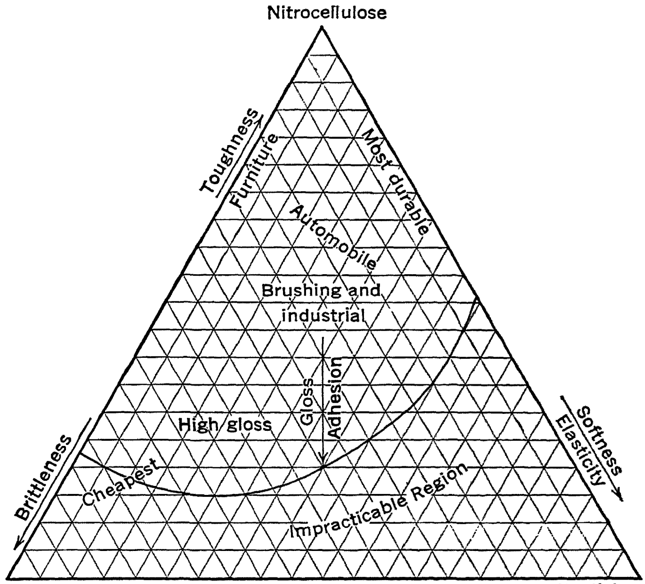


FIG. 57. Relation of components of solids contents to properties of lacquer.

portion is then composed essentially of a cellulose derivative, a resin, and a plasticizer, whereas the volatile portion consists of the solvent and diluents. If the composition of the non-volatile portion is now graphically represented by the use of triangular coordinates and the nature of the films obtainable determined empirically for the various areas on the graph, a chart of the type shown in Fig. 57 results.

From the figure it is seen that as the resin content increases, the durability and toughness decrease, while the gloss, adhesion, and cheapness increase until the composition contains so much resin that it is approaching a spirit varnish. With increase of plasticizer, the lacquer film becomes increasingly soft.

A series of such charts for the various constituent combinations

[11] H. E. Hofmann and E. W. Reid, *Ind. Eng. Chem.*, 20, 431 (1928).

gives the proper amount of cellulose derivative, resin, and plasticizer to produce a film of any given set of properties. Choice of proper solvents and diluents may be made from a study of rectangular coordinate graphs of dilution ratios and evaporation rates for the various lacquer solvent components.

After the composition of the non-volatile portion has been established for the desired film, the volatile portion of the lacquer may be studied graphically, using a triangular coordinate system. Once the areas of insolubility and cloudy and clear films have been outlined empirically, the behavior of solvent mixtures is understood. A solvent and a diluent in a mixture may not dissolve nitrocellulose, but the addition of a second diluent may form a solvent for nitrocellulose. If such a mixture consists originally of equal parts of a solvent and a hydrocarbon, the point on the chart representing this particular mixture is the midpoint of the side between the two components. If alcohol is added, the locus of the point will be the normal to the side of the triangle. If at some point this path passes through the area of clear films, the addition of alcohol results in nitrocellulose solubility.

The addition of a diluent may serve to prevent blushing. Cotton and gum blush occur whenever the evaporation rate of the solvent for either component is sufficiently high to cause the dilution ratio of that component to be exceeded before the film has completely dried. Blushing appears in the chart as areas in which turbid or opaque films are obtained. A diluent may form an azeotropic mixture of uniform evaporation rate.

Precaution against discoloration from contamination by contact with metals during the preparation and storage of the lacquer has been stressed previously in the case of resin solutions.

Damar in Nitrocellulose Lacquers. Damar finds commercial applications in a wide variety of lacquers ranging from nail polishes, corn cures, and pottery lacquers to the lacquers applied as industrial finishes. Damar is employed in lacquers used as metal primers, metal finishes, wood finishes, paper coatings, leather finishes, rubbing lacquers, gloss finishes, industrial and architectural enamels, bronzing fluids, lacquer emulsions, both pigmented and unpigmented, and in the various "dopes" used in the manufacture of artificial leather.

Damar is the palest and lightest of the natural resins. It is easily combined with nitrocellulose in lacquer formulations and imparts high gloss, good flow, and excellent adherence. Damar films are bleached colorless upon exposure to light and thus improve in appearance with duration of time, whereas other resins, which have darker original

colors, usually yellow with age. The damars are non-reactive with alkaline pigments and are, therefore, suitable for lacquer enamels. Light colored damar lacquer enamels show excellent color retention. Damar is one of the few resins suitable for lacquer formulation which is not prohibited for use in food packaging.

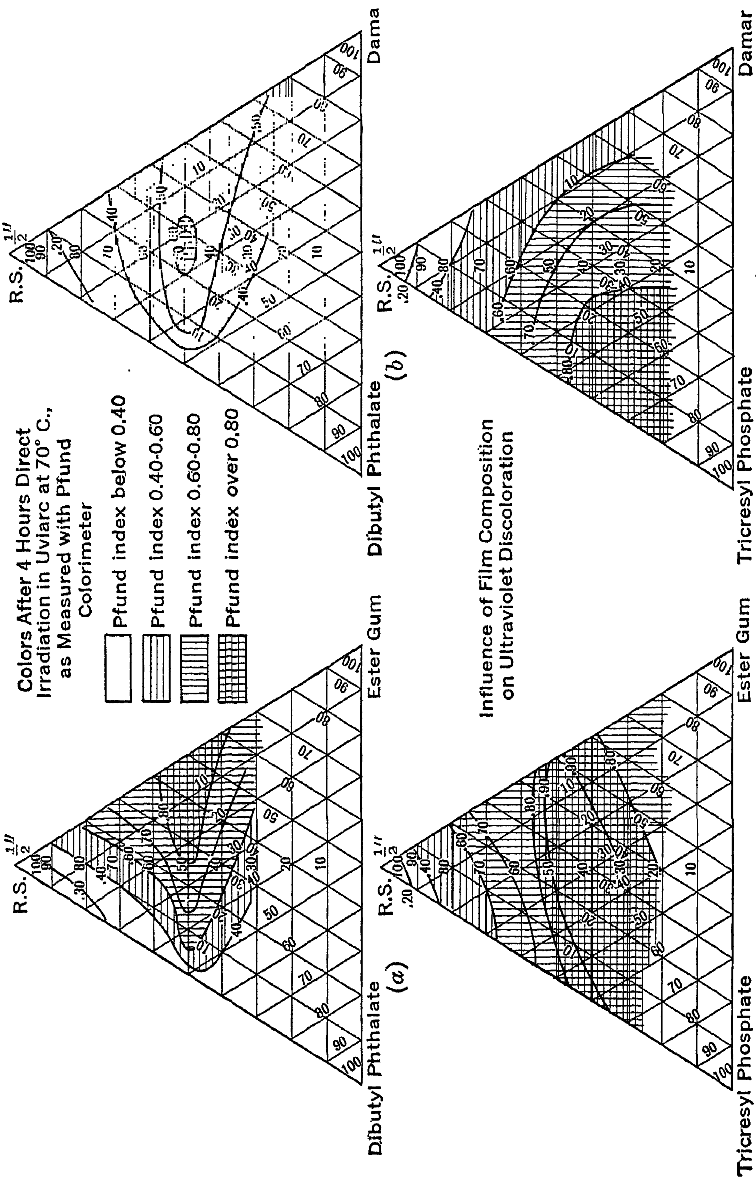
The light-resistant properties of damar in lacquer films have been demonstrated.[12] Changes in the color of uniform lacquer films upon irradiation with ultraviolet light were determined by the Pfund multiple reflection colorimeter. The results were expressed in terms of a color index. Representative plasticizers and resins were examined in this manner using 10 parts of RS ½-second nitrocellulose and 5 parts of the material under test. Ultraviolet irradiation was for a period of 4 hours at 70°C. The results obtained are given in Table C.

TABLE C

Name	Color Index
Plasticizers	
Tributyl phosphate	.11
Tricresyl phosphate	.57
Triphenyl phosphate	.63
Dibutyl phthalate	.14
Dibutyl tartrate	.24
Methylcyclohexyladipate	.13
Methyl-*p*-toluenesulfonamid	.66
Camphor	.35
Raw castor oil	.37
Blown castor oil	.35
Resins	
Ester gum	.66
Damar	.46
Manila elemi	.61
Manila copal	.66
Non-convertible alkyd synthetic resin (1)*	.65
Oxidizing alkyd synthetic resin	.55
Non-convertible alkyd synthetic resin (2)*	.64
Sulfonamid resin	very dark
Phenol-formaldehyde resin	1.06
Polyvinylacetate resin	0.09
Indene type resin	1.06

* The non-convertible alkyd synthetic resins (1) and (2) tested in the above list were made by different manufacturers.

[12] "Relative Effect of Nitrocellulose, Gums, and Plasticizers on Discoloration," *Bull.*, Research Dept. Hercules Powder Co., 1933.



Colors After 4 Hours Direct Irradiation in Uviarc at 70° C., as Measured with Pfund Colorimeter
Pfund index below 0.40
Pfund index 0.40-0.60
Pfund index 0.60-0.80
Pfund index over 0.80
Influence of Film Composition on Ultraviolet Discoloration
R.S. 1/2"
Dibutyl Phthalate
Ester Gum
Dama
Tricresyl Phosphate
Damar
(a)
(b)
(c)
(d)

FIG. 58.

With the exception of the polyvinyl acetate resin, damar gave less discoloration than did any other resin tested. Manila copal, ester gum, and the non-convertible alkyds were about equal, while elemi showed somewhat better results.

The investigation also shows that binary systems of nitrocellulose and plasticizer yield greater discoloration with increasing plasticizer content whereas binary systems containing nitrocellulose and resin show greater discoloration than either component alone. The introduction of a third non-volatile component, even though very resistant in binary mixtures, increased discoloration. If the third component is not resistant to discoloration in binary mixtures, the inclusion of small amounts of such material results in light-sensitiveness in the useful range of formulation nearly as great as with larger amounts of light-sensitive materials.

The discoloration effects of various combinations of damar, ester gum, dibutyl phthalate, and tricresyl phosphate, (the damar and dibutyl phthalate being selected as representative of light-resistant resins and plasticizers and the ester gum and tricresyl phosphate as representative light-sensitive materials) are illustrated in Fig. 58.

Greater discoloration than normal with the use of two light-resistant materials is shown in Fig. 58(*b*). The unexpectedly great discoloration from small quantities of light-sensitive materials is indicated in Fig. 58(*a*) and 58(*d*) by the crowding of the contour lines along the line representing the system containing nitrocellulose and the light-sensitive component only. Figure 58(*c*) illustrates the system in which both resin and plasticizer are light-sensitive. The rate of discoloration during irradiation is shown in Fig. 59.

The practical application of the information furnished by this investigation to clear lacquer formulation has been summarized in the original reference as follows:

> In the manufacture and sale of lacquers, many variables other than those mentioned affect their discoloration, such as the varying conditions in manufacturing and the varying quality of the ingredients used. However, it has been proved that a material which behaves well towards light by itself or in simple mixtures should not be expected to be equally light-resistant when used in more complex mixtures. Also, to obtain lacquers giving minimum discoloration, the number of non-volatile components should be kept at a minimum, and the use of even small quantities of light-sensitive plasticizers and resins should be avoided.

The usual use of the word damar in the literature does not refer to

damar, as such, when used in nitrocellulose lacquers, but to dewaxed damar. The β-resene from damar resin is not compatible with nitrocellulose. Damar which has not been dewaxed may be included in nitrocellulose lacquer formulations in order to produce a flat finish.

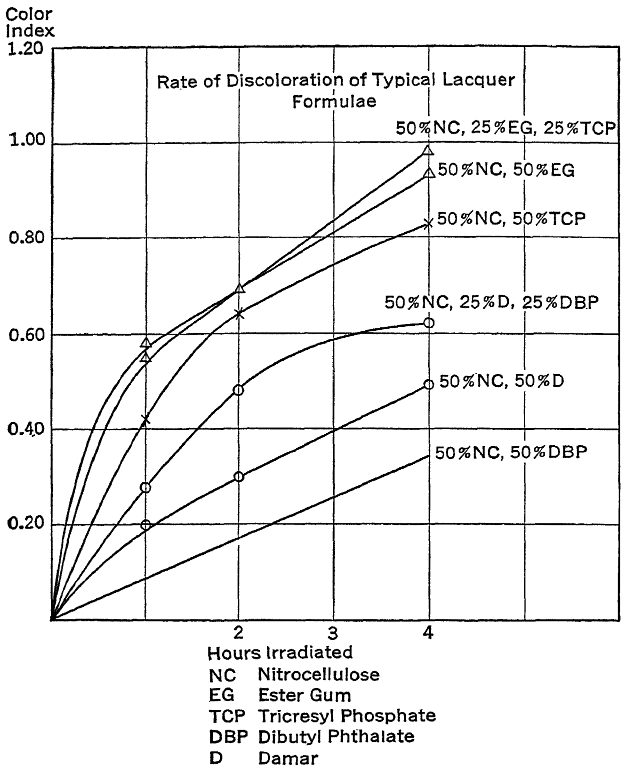


FIG. 59.

Such films tend to be opaque. The dewaxing operation has been described in the chapter on natural resin purification.

The proportion of damar to nitrocellulose varies according to the purpose of the formulation, but a common ratio is 2 parts of damar to 1 part of nitrocellulose. Formulations of higher damar content are used for special purposes, but become damar spirit varnishes to which nitrocellulose has been added to harden the film.

Table CI illustrates varying proportions of damar in nitrocellulose lacquers. The formulations given are unplasticized.

TABLE CI

DAMAR-NITROCELLULOSE LACQUERS

Formula No.	303	304	305	306
Ratio Nitrocellulose to Resin	1 : 2	1 : 3	1 : 1	2 : 1
Dewaxed damar	22 lb.	24 lb.	16.5 lb.	11 lb.
Nitrocellulose—RS (½ sec.)	11 lb.	8 lb.	16.5 lb.	22 lb.
Ethyl acetate	15 lb. (2 gal.)	15 lb.	15 lb.	15 lb.
Butyl acetate	10 lb. (1.37 gal.)	10 lb.	10 lb.	10 lb.
Ethyl lactate	5 lb. (0.58 gal.)	5 lb.	5 lb.	5 lb.
Butanol	5 lb. (0.75 gal.)	5 lb.	5 lb.	5 lb.
Toluol	40 lb. (5.52 gal.)	40 lb.	40 lb.	40 lb.
Xylol	25 lb. (3.45 gal.)	25 lb.	25 lb.	25 lb.

Damar in Clear Lacquers. In studying the value of damar in lacquers, two series of lacquers were made, employing a resin-nitrocellulose ratio of 1 to 2 in the first series and a ratio of 1 to 1 in the second. Throughout each series the formulation was the same for each lacquer except for the type of resin used. The resins used were ordinary dewaxed damar, damar resin acids, α-damar resene, ester gum, two modified-phenolic resins recommended for lacquers, and an alkyd type. In the tests (Table CII), the comparative values given by the one series were duplicated in the tests on the other series. Dewaxed damar ranks higher in these tests than any of the other resins except alkyds. The dewaxed damar gives materially better properties than either of the two fractions of the resin which compose it—the damar acids and the α-damar resene. The lacquers containing damar or damar resin fractions were all bleached to a water-white by the exposure. All the remaining lacquers, originally having a slight coloration, showed a pronounced yellowing during the exposure.

Batu and Pale East India in Nitrocellulose Lacquers. Batu and pale East India resins are used for flat lacquer finishes. Since they are related to the damars, it might be expected that their behavior in

TABLE CII

Resin	Whiteness	Hardness	Resistance to Water	Gloss	Weathering Time First series (*weeks*)	Weathering Time Second series (*weeks*)
Dewaxed damar	2*	1*	2*	All	18	20
Damar acids	8	3	7	about	20	10
α-resene	4	5	6	the	10	7
Ester gum	3	8	4	same	9	8
Manila ester	6	4	1		9	8
Modified phenolic No. 1	5	6	5		9	9
Modified phenolic No. 2	7	7	3		9	8
Alkyd	1	2	8		26	29

* Numerals indicate comparative rank, number one indicating the best properties. Damar bleached to a color equal to 1.

TABLE CIII

Formula No.*	307	308	309	310	311
Nitrocellulose	10	10	10	10	10
Pale east india chips (Macassar)	2	5	5	5	5
Castor oil	2.5	2.5	2.5	2.5	2.5
Dibutyl phthalate	2.5	2.5	2.5	2.5	2.5
Butyl acetate	25 (3.42 gal.)	12 (1.64 gal.)	35 (4.8 gal.)	25 (3.42 gal.)	35 (4.8 gal.)
Cellosolve acetate		16 (1.98 gal.)	5 (0.62 gal.)		5 (0.62 gal.)
Butanol	19 (2.84 gal.)		15 (2.25 gal.)	20 (3 gal.)	15 (2.25 gal.)
Solox		26 (3.9 gal.)		10 (1.5 gal.)	
Ethyl acetate			5 (0.67 gal.)	10 (1.34 gal.)	5 (0.67 gal.)
Toluol	35 (4.83 gal.)	26 (3.59 gal.)	20 (2.76 gal.)	15 (2.07 gal.)	20 (2.76 gal.)

* All lacquers are made by agitating all the ingredients together until homogeneity is achieved. Quantities are in pounds.

lacquer formulations would be similar. In pale east india and batu nitrocellulose formulations a separation appears to be the result of a partial incompatibility on the part of the resin. This incompatibility is responsible for the flatness of the films obtained.

In Table CIII five representative formulations are given. In each the formulation is plasticized with equal parts of dibutyl phthalate and castor oil. Superior lacquers can be produced by the selection of better grades of resin. It is possible to vary the proportion of resin over a wider range than indicated.

Lacquers of the above type may vary considerably in film characteristics. Although usually dull, varying degrees of semi-gloss and, at times, even an appreciable luster may be obtained. A further example of a flat lacquer containing pale east india is as follows:

Formula 312

10 lb. Pale east india bold
10 lb. Nitrocellulose
20 lb. (2.67 gal.) Ethyl acetate
20 lb. (3 gal.) Butanol
40 lb. (5.5 gal.) Hi-flash naphtha

Procedure: Mix and agitate all the ingredients until a homogeneous mixture is obtained.

Formula 312 produces a yellowish-orange colored lacquer which dries to a flat film. Where flat finishes are desired, it is frequently customary to include small amounts of flatting agents such as diatomaceous earth or chlorinated rubber.

As in damars, the slight incompatibility encountered with batu and the pale east indias is the result of the wax content of the resin. By means of a dewaxing operation, similar to that employed in the preparation of damar for lacquer formulation, dewaxed batu and dewaxed pale east india may be prepared. These dewaxed resins, when incorporated in nitrocellulose lacquers, give clear, haze-free films of appreciable luster. The wax content of these resins, however, is higher than that of the damars and the loss resulting from dewaxing is appreciably greater.

The principal use of batu and pale east india lacquers is to be found in the finishing of inexpensive wooden furniture in which varying degrees of dull finish are desired. The low cost of the resin and the dullness of the films obtained make them ideal for this purpose.

Kauri in Nitrocellulose Lacquers. The principal difficulty lies in obtaining the correct solvent balance so that the resulting film will

possess good adherence and be free from cloudiness. When properly formulated, kauri lacquers possess excellent adherence.

The most satisfactory solvents are the esters and alcohols, mixtures with such components as ethyl and butyl acetate and alcohol and butyl alcohol. The inclusion of a hydrocarbon solvent may be found to be advantageous. Typical satisfactory formulations are given in Table CIV.

TABLE CIV

MANILA AND KAURI LACQUERS

Formula No.	313		314		315		316		317		318	
	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.
Nitrocellulose AS $\frac{1}{2}$ sec.	8	...	13–7	...	13	...	10	...	7	...	10	...
Accroides	...	...	...	...	...	...	...	...	...	...	10	...
Manila DBB	...	...	...	...	7	...	...	...	...	...	...	...
Pontianak	...	...	...	...	...	...	10	...	...	...	...	...
Boea hard amber	...	...	...	...	...	...	...	...	13	...	...	...
Bush kauri chips	5	...	...	...	...	...	...	...	...	...	...	...
Pale kauri	...	...	7–13	...	...	...	...	...	...	...	...	...
Cellosolve	...	...	...	...	16	2.06	16	2.06	16	2.06	...	...
Butanol	20	2.96	16	2.37	48	7.11	48	7.11	48	7.11	...	...
Ethanol	...	...	48	7.27	16	2.42	16	2.42	16	2.42	16	2.42
Ethyl acetate	30	4.08	...	...	...	...	...	...	...	...	32	4.35
Butyl acetate	40	5.52	16	2.21	...	...	...	...	...	...	...	...
Tricresyl phosphate	7	...	7	...	...	...	...	...	...	...	32	4.4

Other grades of kauri may be substituted for the bush kauri chips, and the ratio of resin to nitrocellulose may be altered. In such cases, it is necessary to determine experimentally the correct proportions for complete solvent balance. The kauri should be thoroughly dry.

Elemi in Nitrocellulose Lacquers. Elemi, in itself, is too soft to serve as the resinous component of a lacquer, but it does possess excellent properties as a plasticizer.

Its use in the industry is of long duration, dating from before the development of the high-boiling butyl and amyl type of solvents. At that time elemi was included in nitrocellulose lacquers for improving the flow and the ease of brushing.

Elemi confers a high degree of flexibility, which is retained by the lacquer over extended periods of time. It also imparts a high degree of adhesion to smooth surfaces, and is favored in the preparation of clear metal lacquers and bronzing fluids. Although it increases flexibility and adhesion, elemi appreciably softens the lacquer film and

for this reason is frequently found in conjunction with some harder resin. It is usually introduced into the lacquer in a solution containing 6 to 8 pounds per gallon. Proportions vary, but from 5 to 15 per cent by volume as compared to the nitrocellulose solution is generally satisfactory. Rather high percentages of elemi are used for lacquers to be applied to metal surfaces which are subsequently to be sheared or bent.

Manila Copals in Nitrocellulose Lacquers. Since the advent of alcohol-soluble nitrocellulose, the manilas have found broadened fields of application in the lacquer industry. The manilas provide lacquer films of good color and high luster. The films obtained are harder than those from damar-containing lacquers and are better suited for use as sanding sealers and in the finishing of wooden furniture. Manila lacquers do not show quite so good adherence as those made with damar and frequently contain damar, which improves both the gloss and adhesion, or elemi, when greater flexibility is desired.

Table CIV shows three representative formulations containing various grades of manila. Similar formulations containing the softer lobas and melengkets may be prepared. Plasticizers have been omitted but should be included according to the intended application.

Since the manilas do not soften the lacquer film as much as the damars, they may be employed in higher proportions. In addition to furniture finishing, manila lacquers are used for paper coating and leather finishing. They form the basis of cheap enamels of excellent quality when pigmented, providing that the use of reactive pigments be avoided.

Mastic, Sandarac, and Accroides in Nitrocellulose Lacquers. The use of mastic and sandarac in nitrocellulose lacquers has been common since the inception of the industry.

Mastic has been found advantageous in the preparation of lacquers to be applied to porous surfaces. It finds limited use in paper-coating lacquers and in lacquers to be applied over plaster.

Sandarac finds a limited use as a lacquer in photographic work. Both of these resins produce lacquers of very pale color. Sandarac is occasionally used in lacquers for priming metal surfaces. It imparts good adhesion to the lacquer but does not give very satisfactory resistance to weathering.

Accroides finds some use in nitrocellulose lacquers where color is not an important consideration. In such instances its cheapness recommends its use. A suitable unplasticized formula is 318, Table CIV.

Run Congo in Nitrocellulose Lacquers. In work by the authors on the use of run congo in nitrocellulose lacquers, comparative tests were made on four different types of resins: dewaxed Batavia damar A/E, maleic-anhydride-rosin-resin, 100 per cent phenolic resin for lacquers, run hard dark amber congo (congo No. 11).

Lacquers were made with each resin and nitrocellulose with ratios of nitrocellulose to resins of 1 to 2, 1 to 4, 1 to 6, 1 to 8, and 1 to 10. The non-volatile content was 25 per cent by weight for all lacquers and the solvent used consisted of the following mixture for all lacquers except those containing run congo No. 11: ethyl acetate, 15 (parts by weight); butyl acetate, 10; butyl lactate, 5; butanol, 5; xylol, 25; toluol, 40.

For the lacquers containing run congo, the following solvent mixtures were used for each combination as shown (parts by weight). The nitrocellulose was ½ second.

TABLE CV

Ratio nitrocellulose to resin	1 : 2	1 : 4	1 : 6	1 : 8	1 : 10
Ethyl acetate	17.2	7.9	25.5	32.3	34.8
Butyl acetate	11.3	5.2	16.8	21.2	22.8
Butyl lactate	5.7	2.6	8.5	10.8	11.6
Butanol	85.8	75.8	97.2	160.0	214.0
Xylol	43.0	24.5	86.0	75.0	64.8

The solvent mixture had to be varied for each combination of nitrocellulose and run congo, as one solvent combination could not be used for all ratios of nitrocellulose to resin. The properties are given in Table CVI.

Consistent results could not be obtained using the Sward Hardness Rocker, although each value is an average of three tests. The Sward values do not indicate a relationship between the hardness and ratio of nitrocellulose to resin. Values obtained with the Venus pencils show in all cases that the hardness decreases as the ratio of resin to nitrocellulose is increased. In general, run congo produces the hardest films, followed in order by the maleic-anhydride resin, the 100 per cent phenolic, and the dewaxed damar.

The resistances are given in Table CVII. The conclusions were:

1. In resistance to alcohol, dewaxed damar is inferior to the maleic-anhydride resin, the 100 per cent phenolic, and run congo. Except for

TABLE CVI

DATA ON LACQUERS AND LACQUER FILMS

Resin	Formula No.	Ratio of Nitrocellulose to Resin	Sward Hardness No.	Venus Pencil Hardness	Color (G-H)	Viscosity (G-H)	Gloss
Dewaxed Batavia damar A/E	319	1 : 2	47	4H	5	A−	Very high
	320	1 : 4	58	2H	6	A−	Very high
	321	1 : 6	53	2H	6	A−	Very high
	322	1 : 8	65	2H	6	A−	Very high
	323	1 : 10	75	2H	6	A−	Very high
Glycerin-maleic-rosin	324	1 : 2	82	5H	6	A–B	Very high
	325	1 : 4	85	4H	6	A−	Very high
	326	1 : 6	78	4H	6	A−	Very high
	327	1 : 8	75	4H	7	A−	Very high
	328	1 : 10	84	4H	7	A−	Very high
100 per cent phenolic	329	1 : 2	55	6H	1	A−	Very high
	330	1 : 4	49	5H	1	A−	Very high
	331	1 : 6	45	4H	1	A−	Very high
	332	1 : 8	35	3H	1	A−	Very high
	333	1 : 10	42	2H	1	A−	Very high
Run hard dark amber congo (congo No. 11)	334	1 : 2	68	5H	18	B	Very high
	335	1 : 4	77	5H	18	A	Very high
	336	1 : 6	75	5H	18	A−	Very high
	337	1 : 8	67	4H	18	A−	Very high
	338	1 : 10	76	4H	18	A−	Very high

a slight blush, run congo is as good for alcohol resistance as the maleic-anhydride resin and the 100 per cent phenolic resin.

2. The 100 per cent phenolic is superior for caustic resistance. Dewaxed damar, in turn, is superior to the run-congo and maleic-anhydride resin.

3. Dewaxed damar and the 100 per cent phenolic both show very good resistance to boiling water. The maleic anhydride and run congo show poor resistance to boiling water.

4. All showed very good resistance to salt water (20 per cent salt solution) except the maleic-anhydride resin, which was very poor.

5. All the resins showed good resistance to commercial gasoline.

The procedure for running the Congo resin was as follows:

The resin was heated to 650°F. in 1 to 1½ hours, and held until oil and toluol soluble. The loss in running was 25 per cent. The nitrocellulose used in the lacquer formulations was AS ½ second. No plasticizer was used. Suitable plasticizers include dibutyl phthalate, tricresyl phosphate, and similar materials.

TABLE CVII

Resin	Formula No.	Ratio Nitrocellulose to Resin	Liquids: 50 per cent alcohol	Liquids: 5 per cent caustic	Liquids: Boiling water	Liquids: Salt water (20 per cent salt)	Liquids: Gasoline
Dewaxed Batavia damar A/E	319	1 : 2	5M—Turned white 25M—Failed	20M—OK 34 H—Failed	20M—White 8 H—OK	96H—OK	96H—OK
	320	1 : 4		20M—White 34 H—Failed		"	"
	321	1 : 6		20M—White 34 H—Failed		"	"
	322	1 : 8		20M—White 96 H—OK		"	"
	323	1 : 10				"	"
Glycerin-maleic-rosin	324	1 : 2	96 H—OK	3½H—Failed	20M—White 40M—Failed	48H—Failed	96H—OK
	325	1 : 4	"	"		"	"
	326	1 : 6	"	"		"	"
	327	1 : 8	"	"		"	"
	328	1 : 10	"	"		"	"
100 per cent phenolic	329	1 : 2	96H—OK	20M—OK 96 H—OK	20M—White 8 H—OK	96H—OK	72H—Sl. W. 96H—OK
	330	1 : 4	"	Same as for No. 329 except that films were white		"	
	331	1 : 6	"			"	
	332	1 : 8	"			"	
	333	1 : 10	"			"	
Run hard dark amber congo (congo No. 11)	334	1 : 2	40M—Sl. blush 96 H—OK	10H—Failed	35M—Failed by blistering	96H—OK	25M—Sl. blush 96 H—OK
	335	1 : 4				"	
	336	1 : 6		"		"	
	337	1 : 8		"		"	
	338	1 : 10		" "		"	

H Hours M Minutes Sl. W. Slightly white

Congo Esters in Nitrocellulose Lacquers. Congo esters are compatible with nitrocellulose. They provide hard, glossy, adherent lacquer films of improved resistance to water, alkali, and acid. The copal esters are non-reactive and are, therefore, suitable for use in lacquer enamels containing alkaline pigments. In baked films they retain both their adhesion and flexibility. Congo ester lacquers are particularly adapted to finishing the interior surfaces of food containers as they

impart no taste or odor to the contents. Fruit acids, sugar solutions, and aqueous food extracts show no effect upon the baked films.

Formulations for esterified congo lacquers are, in general, similar to those of ester gum. The solvents consist of esters, alcohols, and aromatic hydrocarbons.

Gloss Lacquers. Although the inclusion of resins enhances the gloss of cellulosic lacquers, the attainment of high gloss is not so easily accomplished as with oil varnishes. Nitrocellulose films are inherently flat and a number of factors exert an influence on the degree of gloss obtained. Aside from the nature of the resin the more important of these are the percentage of plasticizer, the relative proportion of high- and low-boiling solvents, and the atmospheric conditions during the drying period.

The gloss of a lacquer film is dependent upon the ability of the lacquer to flow out to a thin film prior to complete drying. This ability to flow out is, in turn, a function of the combined plasticizing effect exerted by the resin, plasticizer, and high-boiling solvents. Inclusion of a relatively large proportion of high-boiling solvents permits this leveling action to occur. Gloss may be secured by increased resin content rather than by an increased proportion of solvents of low evaporation rate. Resin to nitrocellulose ratios of 2 to 1 are common.

Metal Primers and Lacquers. Clear metal lacquers serve three purposes. They may be applied directly to the metal surface to protect the metal and improve its appearance, or they may be used as the priming and finishing coats on metal surfaces to be enameled or bronzed.

Lacquers are usually applied to metal in thin films, and high resin content is, therefore, desirable to give maximum solids content with minimum viscosity. Lacquers to be applied to silver are exceptions in that they employ smaller amounts of resin—usually damar. Elemi imparts flexibility to lacquers which are to be applied to metal prior to a bending, shearing, or forming operation.

Priming lacquers are applied to iron, steel, and aluminum surfaces which are subsequently to be printed, bronzed, or enameled. The resin content of these priming coats is usually high to provide good adherence to the smooth surface. The enamel should contain a minimum of solvents for the resin in the primer, as it is desirable that only the surface of the primer be softened to provide bonding between the coats. A suitable priming lacquer for cast iron or steel is included in Table CVIII.

Lacquers are utilized in the protection of copper alloys, such as

brass and bronze. Higher resin contents are used than for silver lacquers, and the lacquer may also be made to enhance the color of the alloy by the inclusion of a soluble dye.

Metal lacquers protect tarnishable metal surfaces such as metal trays, vanity cases, costume jewelry, lighting fixtures, spun brass articles, steel hardware, and articles which have been electroplated. A typical brass lacquer formulation is given in Table CVIII.

Finishing lacquers, as a rule, contain a greater proportion of nitrocellulose, usually low viscosity, than lacquers applied directly to metal surfaces. They are prepared for gloss, semi-gloss, and dull finishes, as desired, the resin content increasing with the gloss. Where extreme durability is desired the gloss lacquer may be over-coated with a flat lacquer of low resin content without destroying the gloss of the finish.

Bronzing Fluids. Damar and elemi are the natural resins usually employed in bronzing fluids. The lacquer is prepared from medium or high viscosity nitrocellulose known as "bronzing cotton" and is usually fairly viscous in order to maintain a uniform pigment dispersion. The resin content is ordinarily kept low. The pigment is usually a copper powder which may be tinted to various shades by the inclusion of dyes. Since copper tends to gelatinize nitrocellulose solutions, the bronze is added just prior to application. The lacquer constituents must be chemically neutral as acidity causes discoloration of the pigment. A typical formulation is given in Table CVIII.

Sanding Sealers. In lacquer-finishing furniture it is necessary that the grain of the wood be filled by the application of a sealer. The constituents of the sanding sealer should show a high rate of solvent release in order that the interval between the application of the sealer and the sanding operation may be minimized. The manilas are low solvent retention resins and are used in nitrocellulose lacquer sanding sealers. Satisfactory sealers may be prepared with damar, but the high solvent retention of the resin necessitates a protracted drying period before sanding. Sanding sealers may also be prepared with combinations of ethyl cellulose and natural resins.

The solids content of sanding sealers usually varies between 20 and 30 per cent, with the ratio of resin to nitrocellulose 1½ or 2 to 1. The choice of solvents varies according to the method of application and the porosity of the surface to be treated. High-boiling solvents are usually maintained at the minimum proportion consistent with ease of application.

Wood Lacquers. The viscosity of wood-finishing lacquers is kept high in order to prevent penetration. The beauty of the finish is a

TABLE CVIII

METAL LACQUERS

Formula No.	339		340		341		342		343	
Type of Lacquer	Metal priming lacquer		High-grade brass lacquer		Gloss finishing lacquer		Dull finishing lacquer		Flexible bronzing liquid	
	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.
Nitrocellulose, R.S. high viscosity	...	...	...	...	4.7	...	4.3	...	4.6	...
Nitrocellulose, R.S. med. viscosity	6.4	...	5.8	...	...	...	...	...	...	...
Nitrocellulose, R.S. ½ sec.	...	...	...	...	4.7	...	5.8	...	...	...
30% Dewaxed damar solution	6.4	...	16.6	...	11.9	...	5.6	...	...	...
50% Dewaxed shellac solution	...	...	...	...	6.0	...	...	...	...	...
50% Ester gum solution	3.2	...	...	...	...	...	...	...	...	...
50% Elemi solution	3.2	...	...	...	...	...	...	...	6.4	...
Dibutyl phthalate	...	...	...	...	0.7	...	1.5	...	...	...
Castor oil	...	...	...	...	...	...	...	...	...	...
Ethyl acetate	11.8	1.6	...	...	5.7	0.71	...	...	22.7	3.09
Butyl acetate	11.7	1.6	26.3	3.62	16.8	2.32	21.1	2.91	...	...
Butyl propionate	...	...	...	...	5.6	0.77	5.2	0.71	...	...
Denatured alcohol	5.3	0.8	...	...	...	...	...	...	...	...
Butanol	5.4	0.8	9.7	1.44	10.4	1.54	9.7	1.44	5.2	0.77
Benzol	23.5	3.22	...	...	...	...	...	...	33.7	4.62
Toluol	23.1	3.19	41.6	5.74	33.5	4.62	46.8	6.47	16.6	2.29
Acetone	...	...	...	...	...	...	...	...	10.1	1.52

function of the depth of film. Low-viscosity nitrocellulose is employed so that a maximum film thickness may be obtained with a minimum of applications. The resin content of wood lacquers is higher than for any other type. The lacquer is in reality a spirit varnish to which a small amount of nitrocellulose has been added to harden the film. The formulae of two typical wood lacquers are given in Table CIX. The high-viscosity nitrocellulose aids in the prevention of sagging on vertical surfaces during the drying period. The urea is a color stabilizer.

High polishes can be obtained by mechanical rubbing. Flat or semigloss finishes are made by incorporating small amounts of transparent

flatting agents, such as the aluminum, magnesium, and zinc stearates, or silica, diatomaceous earth, and magnesium carbonate.

Wood lacquers are used in the manufacture of small items such as lead pencils, brush and broom handles, dolls, canes, and miscellaneous children's toys and games.

Leather Finishes. The use of resins in the preparation of artificial leather, split leather, and patent leather is somewhat limited. Damar (dewaxed), elemi, mastic, sandarac, and the manilas are used. The general practice is to include resins in the priming coat to improve adhesion and in the finishing coat to supply gloss. The minimum of resin is used in order to avoid brittleness. Dewaxed damar and elemi

TABLE CIX

	Wood lacquer		Leather finishing
Formula No.	344	345	346
Stock celluloid*	...	...	180
Nitrocellulose ($\frac{1}{2}$ second)	11.0 lb.	13.8 lb.	...
Nitrocellulose (high viscosity)	3.5 lb.	4.1 lb.	...
Dewaxed damar	...	...	17
30 per cent dewaxed damar solution	21.7 lb.	5.3 lb.	...
50 per cent ester gum solution	9.0 lb.	...	...
Dewaxed shellac solution in butanol	...	5.3 lb.	...
Ethyl acetate	5.2 lb.	...	...
	(0.77 gal.)	...	...
Amyl acetate	...	5.0 lb.	60
	...	(0.69 gal.)	...
Butyl acetate	10.2 lb.	20.1 lb.	60
	(1.4 gal.)	(2.88 gal.)	...
Butanol	11.8 lb.	9.4 lb.	30
	(1.4 gal.)	(1.39 gal.)	...
Toluol	25.4 lb.	34.8 lb.	50
	(3.5 gal.)	(4.8 gal.)	...
Tricresyl phosphate	2.0 lb.	...	...
Dibutyl tartrate	...	...	5
Dibutyl phthalate	...	2.0 lb.	...
Benzyl benzoate	...	...	15
Urea	0.2 lb.	0.2 lb.	...
Rapeseed oil	...	...	10
Camphor	...	...	9

* 2-lb. cut of scrap film in methanol and acetone.

seem to be usually preferred. A finishing coat containing dewaxed damar is given in formula 346, Table CIX.

Paper-Coating Lacquers. The use of lacquers in paper coating has several advantages but is more expensive than the common practice of spirit varnishing. The lacquer films for this purpose are hard, glossy, flexible, transparent, and more durable than the spirit-varnish films. They must not tend to soften at slightly elevated temperatures nor exhibit residual tack. Damar, the manilas and elemi are the natural resins most used. Formulations vary widely in accordance with such factors as the porosity of the stock and the rates and methods of application and drying.

Lacquer Enamels. The inclusion of pigments in lacquer formulations results in increased brittleness and decreased adhesion. These adhesion difficulties may be overcome by the use of a priming coat. The inclusion of a resin and a plasticizer in the enamel is necessary. Dewaxed damar is non-reactive with alkaline pigments and provides good gloss, adherence and resistance to after-yellowing. Elemi may be used as a plasticizer.

The common method of preparing lacquer enamels is by grinding in a ball mill. The resin is introduced as a solution which has previously been dewaxed. Typical formulations are given in Table CX.

Miscellaneous Lacquers. A large variety of lacquers containing natural resins are utilized for miscellaneous minor applications, such as toy lacquers, nail polishes, pottery lacquers, and tumbling and dipping lacquers. The ordinary nail polishes are nitrocellulose lacquers to which a dye has been added.

Lacquer Emulsions. Nitrocellulose lacquers in the form of aqueous emulsions have been patented.[13] Briefly, the method comprises the emulsification of a viscous, high solids content lacquer with water as the external phase. The emulsions may be pigmented or clear and may be applied by spraying, brushing, dipping, or with a coating machine.

Among the advantages claimed are reduction of cost through application of a greater weight of solids with any given quantity of solvent, reduction of the normal fire hazard, and decreased penetration when applied to porous surfaces.

Suitable natural resins are dewaxed damar, mastic, and elemi. With dewaxed damar it was found necessary to use either water-wet or butanol-dampened nitrocellulose as the water-miscible alcohol content of the nitrocellulose and the dewaxed damar solution, when combined,

[13] "Lacquer Emulsions," *Bull.*, Hercules Powder Co., 1937.

TABLE CX

LACQUER ENAMELS

Formula No.	347		348		349		350	
Type of Enamel	Egg-shell white		Sprayed gloss white		Maroon		Blue	
	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.
Zinc oxide	11.2*	...	2.6	...	...	...	2.2	...
Titanium dioxide	6.8	...	10.3	...	...	...	...	...
Venetian red	...	...	...	...	7.0	...	...	...
Para toner	...	...	...	...	1.2	...	...	...
Prussian blue	...	...	...	...	7.0	...	11.9	...
Chrome green	...	...	...	...	...	...	5.4	...
Nitrocellulose, R.S. high viscosity	2.2	...	2.6	...	2.4	...	2.2	...
Nitrocellulose, R.S. $\frac{1}{2}$ sec.	10.2	...	5.1	...	14.1	...	17.2	...
30% Dewaxed damar solution	17.0	...	29.8	...	17.8	...	12.4	...
Dibutyl phthalate	...	...	3.9	...	...	...	6.5	...
Tricresyl phosphate	4.5	...	...	...	...	...	...	...
Butyl acetate	16.3	2.23	9.3	1.28	17.1	2.34	7.8	1.07
Amyl acetate	...	...	...	...	...	...	7.8	1.09
Butanol	7.6	1.13	8.7	1.30	8.0	1.19	11.1	1.66
Toluol	24.2	3.36	27.7	3.83	25.4	3.52	15.5	2.15

* White seal.

was sufficient to cause a tendency toward instability. Typical formulations are reproduced in Table CXI. Lacquer emulsions are applicable to many of the common uses but are recommended as particularly adapted to paper and textile coating, wood finishing, and the manufacture of adhesives.

Cellulose Acetate Lacquers. With the exception of accroides, all the natural resins show incompatibility with cellulose acetate both with and without thermal processing. Elemi, mastic, and sandarac show only slight incompatibility. Using dioxane as the solvent, accroides can be incorporated in cellulose acetate lacquers in widely varying proportions. Typical formulations are included in Table CXII.

The limited solubility and miscibility of cellulose acetate with lacquer ingredients does not permit of much latitude in the formulation of lacquers.

Ethyl Cellulose Lacquers. Of the cellulose esters and ethers, ethyl cellulose ranks second in volume consumed by the lacquer industry.

TABLE CXI

PIGMENTED LACQUER EMULSIONS

Formula No.	351	352
Color	Black	Gray
Lacquer phase		
Nitrocellulose R.S. ½ sec. (dry)	20.0	18.0
Dewaxed damar (dry)	6.0	5.4
Dibutyl phthalate	3.0	...
Tricresyl phosphate	2.6	3.0
Blown castor oil	5.4	6.0
Carbon black	2.0	...
Gray pigment*	...	12.0
Butanol (carried by nitrocellulose)	8.6	7.8
Butanol	5.0	1.9
Denatured ethanol (in damar solution)	4.0	4.0
High flash naphtha	13.8	14.0
Toluol (in damar solution)	2.0	2.0
Secondary hexyl acetate	13.8	13.0
Octyl acetate	13.8	12.9
Water phase		
Water	98.50	98.20
Duponol M. E. (dry)	0.25	0.25
Sulfonated castor oil	1.25	1.25
Methyl cellulose	...	0.30
Recommended ratio of lacquer phase to water phase (parts by weight)	2.5 : 1 to 3 : 1	2 : 1 to 2.5 : 1

* Composition of gray pigment

Zinc oxide	96.0
Chrome yellow	0.6
Carbon black	0.7
Prussian blue	0.7
Iron oxide	1.0

TABLE CXII

Formula No.	353	354	355
Accroides	8 lb.	14 lb.	20 lb.
Cellulose acetate	16 lb.	14 lb.	10 lb.
Dioxane	76 lb. (8.83 gal.)	77 lb. (8.95 gal.)	70 lb. (8.14 gal.)

Mix all ingredients together until a uniform product is obtained. The solution and dried film are clear.

It is soluble in a wide range of solvents, including hydrocarbon solvents, and produces tough, durable films of low flammability.

With the exception of accroides, batu, and the east indias, which exhibit some incompatibility, all the natural resins find use in ethyl cellulose lacquers. Damar may be used without the necessity for dewaxing. Ethyl cellulose lacquers may be readily prepared with run congo and with all of the thermally processed resins which did not show incompatibility prior to the running operation.

Transparent, glossy, haze-free lacquers can be obtained from raw congo dust. A suitable formulation is as follows:

Formula 356—Congo-Ethyl Cellulose Lacquer

10 lb. congo dust (congo No. 28)
10 lb. ethyl cellulose
40 lb. (6 gal.) anhydrous ethyl alcohol
20 lb. (3 gal.) isopropyl alcohol
20 lb. (2.98 gal.) methyl propyl ketone

In application a plasticizer should be added. Two methods of preparation give satisfactory results. The congo dust may be dissolved in the isopropyl alcohol and methyl propyl ketone by agitation in a ball mill. The solution is then centrifuged to remove suspended matter and the clear solution added to a solution of ethyl cellulose in anhydrous ethyl alcohol. The lacquer may also be prepared by grinding all the ingredients together in a ball mill and centrifuging the resulting solution. Ethyl cellulose shows interesting possibilities for the use of raw congo in lacquers inasmuch as the congo dust solution shows a slight incompatibility with nitrocellulose.

The Hercules Powder Company[14] has made an extensive investigation for the purpose of evaluating the various types of resins and plasticizers for use in ethyl cellulose lacquers. In the valuation of resins, six lacquers were prepared for each resin tested. Three of these lacquers were prepared with a resin to ethyl cellulose ratio of 1 to 2 while the other three contained resin and ethyl cellulose in equal proportions. For each ratio there was an unplasticized formulation, a formulation plasticized with dibutyl phthalate and a formulation plasticized with raw castor oil (AA). The lacquer films obtained were tested for adhesion to various surfaces; resistance to water, alkali, acid, and salt solutions; hardness; flexibility; adhesion; approximate elongation; gloss; sanding; rubbing; resistance to temperature change;

[14] "Ethyl Cellulose-Resin-Plasticizer Mixtures," *Bull.*, 1938.

and discoloration. The formulations used and the results obtained are shown in Table CXIII.

In the preceding investigation mastic was found to give poor adherence with ethyl cellulose and was eliminated for that reason.

In the evaluation of plasticizers, formulations were prepared containing selected resins representative of the various types. Loba A was chosen as the representative natural resin. The resin and ethyl cellulose were present in equal proportions in all of the lacquers prepared. Eleven plasticizers were tested using 10, 20, and 30 per cent of plasticizer on the weight of the ethyl cellulose. The resulting lacquers were subjected to the same tests as the lacquers given in Table CXIII. The results obtained are shown in Table CXIV.

With the aid of the preceding tables it is possible to select the most suitable plasticizer and natural resin for any given set of conditions. Specific properties may then be altered by varying the proportions of the constituents.

An investigation has been made of the effect upon hardness, moisture resistance, and resistance to cold check and abrasion obtained by the incorporation of ethyl cellulose in pontianak and manila DBB spirit varnishes.[15] Standard ethyl cellulose (20 centipoise viscosity) was substituted in 5 per cent increments for 0 to 25 per cent of the resin content in a 3-lb. resin cut. The solvent consisted of 75 per cent alcohol and 25 per cent toluol by volume. The results of tests upon the lacquer films are given in Table CXV.

Abrasion resistance is reported in terms of the weight of sand necessary to wear through the film when poured upon the panel, inclined at an angle of 45 degrees, through a vertical tube.

The incorporation of ethyl cellulose in manila spirit varnishes is suggested for the preparation of improved label and carton finishes and as a possible means of increasing the durability of spirit-type traffic paints.

Cellulose Acetobutyrate Lacquers. Cellulose acetobutyrate is a lacquer constituent developed by the Hercules Powder Company and marketed under the trade name of "Hercose C." In its properties it is somewhat similar to cellulose acetate, but possesses a wider range of solubility and is more readily compatible with resins and plasticizers. The Research Department of the same campany has also carried on experimental work on the use of cellulose acetobutyrate in lacquer formulations.[16]

[15] R. C. Ernst, J. B. Tepe, and I. W. Hutchison, Jr., *Ind. Eng. Chem.*, **32**, 1539-40 (1940).

[16] "Hercose C (Cellulose Acetobutyrate)," *Bull.*, 1936.

TABLE

Formula No.	357	358	359	360	361	362
	Thermally processed boea					
	1	2	3	4	5	6
Ethyl cellulose (L.V.), lb.	10	10	10	10	10	10
Resin, lb.	5	5	5	10	10	10
Dibutyl phthalate, lb.	...	1.5	...	...	2.0	...
Raw castor oil, lb.	...	...	2.25	...	...	3
Butanol, lb.	36	36	36	36	36	36
(gal.)	(5.38)	(5.38)	(5.38)	(5.38)	(5.38)	(5.38)
Xylol, lb.	24	24	24	24	24	24
(gal.)	(3.17)	(3.17)	(3.17)	(3.17)	(3.17)	(3.17)
Toluol, lb.	...	...	...	...	...	...
(gal.)	...	...	...	...	...	...
Alcohol, lb.	...	...	...	...	...	...
(gal.)	...	...	...	...	...	...
Compatibility	C	C	C	VSI	VSI	VSI
Adhesion to:						
Steel	G	G	G	G	G	G
Copper	G	G	G	G	G	G
Aluminum	F	G	G	F	G	G
Tin plate	F	G	G	G	G	G
Zinc	G	G	G	G	G	G
Rubber	F	F	F	F	F	F
Cellophane (untreated)	F	G	G	Br.	Br.	Br.
Wood (filled)	F	P	P	G	G	G
Plaster	G	G	G	G	G	G
Glass	G	G	G	G	G	G
Sensitivity to:						
Water	BR B Blis.	BR B Blis.	SR Blis.	SR Blis.	SR S Blis.	SR VS Blis.
5% NaCl solution	SR	SR	VSR	VSR	VVSR	VVSR
5% HCl solution	R	SR	SR	SR	R	VSR
5% NaOH solution	Dis.	Dis.	Dis.	Dis.	Dis.	Dis.
Sward hardness	72	72	72	72	74	74
Flexibility—mandrel	Br.	Fl.	Fl.	Br.	Br.	Br.
Adhesion—mandrel	P	P	P	P	P	P
Approximate elongation—mandrel	<3%	<3%	<3%	<3%	<3%	<3%
Gloss	P	F	F	P	F	F
Sanding	G	F	F	G	G	G
Rubbing	G	G	G	G	G	G
Temperature change—cycles	13	4	2	1	1	1
Discoloration	S	S	S	Mod.	Mod.	S

I	Incompatible	S	Slight
C	Compatible	V	Very
G	Good	R	Rusted
F	Fair	Blis.	Blistered
P	Poor	T	Temporary
Mod.	Moderate		

CXIII

363	364	365	366	367	368	369	370	371	372	373	374
Dewaxed Batavia damar						Elemi					
1	2	3	4	5	6	1	2	3	4	5	6
10	10	10	10	10	10	10	10	10	10	10	10
5	5	5	10	10	10	5	5	5	10	10	10
...	1.5	...	...	2.0	...	...	1.5	...	...	2.0	...
...	...	2.25	...	...	3.0	...	...	2.25	...	...	3.0
...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...
48	48	48	48	48	48	48	48	48	48	48	48
(6.62)	(6.62)	(6.62)	(6.62)	(6.62)	(6.62)	(6.62)	(6.62)	(6.62)	(6.62)	(6.62)	(6.62)
12	12	12	12	12	12	12	12	12	12	12	12
(1.8)	(1.8)	(1.8)	(1.8)	(1.8)	(1.8)	(1.8)	(1.8)	(1.8)	(1.8)	(1.8)	(1.8)
C	C	C	C	C	C	C	C	C	C	C	C
F	P	P	G	F	P	P	P	P	F	G	G
G	G	G	F	G	G	P	P	P	F	G	G
G	P	P	G	P	P	P	P	P	G	P	P
F	P	P	F	P	P	F	P	P	G	F	F
G	G	G	G	G	G	P	P	P	G	G	G
P	P	P	P	P	P	P	P	P	P	P	P
F	P	P	Br.	Br.	P	P	P	P	Br.	P	P
P	P	P	F	P	P	P	P	P	G	P	P
G	F	P	G	G	G	P	P	P	F	P	P
F	P	P	F	P	P	F	P	P	F	P	P
R Blis.	SR S Blis.	VSR VS Blis.	VSR VS Blis.	STBl.	STBl.	Eliminated Poor Adhesion			VS Blis. VSTBl.	VST Bl.	VST Bl.
ST	VVSR	VVSR	VVSR	OK	OK				VVS Blis.	OK	OK
VVSR	OK	VSR	VVSR	OK	OK				VVSR	VVSR	OK
VVSR	SR	VVSR	VSR	Dis.	Dis.				VSR	VVSR	OK
82	70	60	84	70	64				72	62	50
Fl.	V Fl.	V Fl.	Br.	Br.	Br.				Br.	V Fl.	V Fl.
P	F	F	P	P	P				P	F	F
<3%	>30%	>30%	<3%	<3%	<3%				<3%	>30%	>30%
G	G	G	G	G	G				G	G	F
F	P	P	G	P	P				F	P	P
F	F	F	F	P	P				P	P	P
35	31	25	5	20	2				25	29	15
VS	VS	VS	S	S	S				None	None	None

Bl. Blush
BR Badly rusted
Br. Brittle, breaks on bending
Fl. Flexible
< Less than
> More than
Ex. Excellent
So. Softened
Sw. Swollen
Dis. Film disintegrated; complete failure

TABLE CXIII

Formula No.	375	376	377	378	379	380
	Kauri					
	1	2	3	4	5	6
Ethyl cellulose (L.V.), lb.	10	10	10	10	10	10
Resin, lb.	5	5	5	10	10	10
Dibutyl phthalate, lb.	...	1.5	...	...	2.0	...
Raw castor oil, lb.	...	...	2.25	...	...	3.0
Butanol, lb.	36	36	36	36	36	36
(gal.)	(5.38)	(5.38)	(5.38)	(5.38)	(5.38)	(5.38)
Xylol, lb.	24	24	24	24	24	24
(gal.)	(3.17)	(3.17)	(3.17)	(3.17)	(3.17)	(3.17)
Toluol, lb.	...	...	...	...	...	...
(gal.)	...	...	...	...	...	...
Alcohol, lb.	...	...	...	...	...	...
(gal.)	...	...	...	...	...	...
Compatibility	C	C	C	C	C	C
Adhesion to:						
Steel	G	P	P	G	F	F
Copper	G	G	G	G	G	G
Aluminum	P	P	P	P	P	P
Tin plate	P	P	P	P	P	P
Zinc	G	G	G	G	G	G
Rubber	P	P	P	P	P	P
Cellophane (untreated)	P	P	P	P	Br.	Br.
Wood (filled)	P	P	P	F	G	P
Plaster	P	P	P	F	G	G
Glass	P	G	F	G	G	G
Sensitivity to:						
Water	VSR S Blis.	VSR Blis.	VSR Blis.	SR Blis.	VS Blis.	T Bl.
5% NaCl solution	VVSR	OK	OK	VVSR	OK	SR S Blis.
5% HCl solution	VVSR	OK	VVSR	VVSR	VVSR	VVSR
5% NaOH solution	VVSR	VVSR	VVSR	VSR	So. Sw. B Blis.	So. Sw. B Blis.
Sward hardness	72	66	62	72	66	62
Flexibility—mandrel	V Fl.	V Fl.	V Fl.	Br.	Br.	Br.
Adhesion—mandrel	F	G	G	P	P	P
Approximate elongation—mandrel	8%	>30%	10%	<3%	<3%	<3%
Gloss	G	G	G	Ex.	Ex.	Ex.
Sanding	G	G	F	G	G	G
Rubbing	G	G	G	G	G	G
Temperature change—cycles	50+	35	30	20	18	2
Discoloration	None	None	None	VS	VS	None

I	Incompatible	S	Slight
C	Compatible	V	Very
G	Good	R	Rusted
F	Fair	Blis.	Blistered
P	Poor	T	Temporary
Mod.	Moderate		

(Continued)

381	382	383	384	385	386	387	388	389	390	391	392
Macassar manila WS—soft						Manila loba A					
1	2	3	4	5	6	1	2	3	4	5	6
10	10	10	10	10	10	10	10	10	10	10	10
5	5	5	10	10	10	5	5	5	10	10	10
...	1.5	...	...	2.0	...	...	1.5	...	...	2.0	...
...	...	2.25	...	...	3.0	...	...	2.25	...	...	3.0
36	36	36	36	36	36	36	36	36	36	36	36
(5.38)	(5.38)	(5.38)	(5.38)	(5.38)	(5.38)	(5.38)	(5.38)	(5.38)	(5.38)	(5.38)	(5.38)
24	24	24	24	24	24	24	24	24	24	24	24
(3.17)	(3.17)	(3.17)	(3.17)	(3.17)	(3.17)	(3.17)	(3.17)	(3.17)	(3.17)	(3.17)	(3.17)
...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...
C	C	C	C	C	C	C	C	C	C	C	C
F	G	F	G	G	G	G	G	G	G	G	G
G	G	G	G	G	G	G	G	G	G	G	G
P	P	P	P	P	P	P	P	P	P	F	P
P	P	P	P	P	P	P	P	P	P	P	P
G	G	G	G	G	G	G	P	P	G	G	G
P	P	P	P	P	P	P	P	P	P	P	P
P	P	P	Br.	Br.	P	P	P	P	Br.	Br.	P
P	P	P	F	F	F	P	P	P	G	F	G
G	G	G	G	G	G	P	P	P	G	G	G
P	P	P	F	P	P	P	P	P	P	P	P
SR	VSR	VS	VSR	T	VS	SR	VS	VS	VSR	VS Blis.	S Blis.
Blis.	Blis.	Blis.	S Blis.	Bl.	Blis.	Blis.	Blis.	Blis.	STBl.	STBl.	STBl.
VST	VST	VST	VST		BT		ST	ST			
Bl.	Bl.	Bl.	Bl.		Bl.		Bl.	Bl.			
VVSR	OK	OK	VSR	VVS	VVS	VSR	OK	VVSR	VVS	VVSR	VVSR
			S Blis.	Blis.	Blis.				Blis.	VVSBlis.	VVSBlis.
VVSR	OK	VVSR	VVSR	VSR	OK	VVSR	VVSR	VVSR	VVSR	VVSR	OK
So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.
B Blis.	B Blis.	B Blis.	B Blis.	B Blis.	B Blis.	B Blis.	B Blis.	B Blis.	B Blis.	B Blis.	B Blis.
72	64	58	72	64	56	72	64	58	72	70	64
Fl.	V Fl.	V Fl.	Br.	Br.	Br.	Fl.	Fi.	Br.	Br.	Br.	Br.
F	F	F	P	F	F	P	P	F	F	F	F
<3%	4%	>30%	<3%	<3%	<3%	<3%	<3%	<3%	<3%	<3%	<3%
G	G	G	Ex.	Ex.	Ex.	Ex.	Ex.	Ex.	Ex.	Ex.	Ex.
G	F	P	G	F	P	G	F	F	G	G	G
G	G	G	G	G	G	G	G	G	G	G	G
25	20	50+	13	20	4	25	16	15	13	5	2
None	None	None	VS	VS	VS	None	None	None	None	VS	VS

Bl. Blush
BR Badly rusted
Br. Brittle, breaks on bending
Fl. Flexible
< Less than
> More than
Ex. Excellent
So. Softened
Sw. Swollen
Dis. Film disintegrated; complete failure

TABLE

Formula No.	393	394	395	396	397	398
	Chlorinated diphenyl			Pale blown castor oil		
	1	2	3	1	2	3
Ethyl cellulose, lb.	10	10	10	10	10	10
Manila loba A, lb.	10	10	10	10	10	10
Plasticizer, lb.	1	2	3	1	2	3
Butanol, lb.	48	48	48	48	48	48
(gal.)	(7.2)	(7.2)	(7.2)	(7.2)	(7.2)	(7.2)
Xylol, lb.	32	32	32	32	32	32
(gal.)	(4.4)	(4.4)	(4.4)	(4.4)	(4.4)	(4.4)
Adhesion to:						
Steel	G	G	G	F	P	P
Copper	G	G	G	F	F	G
Aluminum	P	F	G	P	P	P
Tin plate	F	F	F	P	P	P
Zinc	G	G	G	F	P	P
Rubber	Br.	Br.	Br.	Br.	Br.	Br.
Cellophane (untreated)	Br.	Br.	P	Br.	Br.	F
Wood (filled)	G	G	G	P	P	P
Plaster	G	G	G	F	P	P
Glass	F	G	G	P	P	P
Sensitivity to:						
Water	VVSR	VVSR VVSBlis.	VSR VSBlis.	VSR	TBl.	SR TBl.
5% NaCl solution	OK	OK	VVSR	OK	OK	OK
5% HCl solution	OK	VVSR	VVSR	VVSR	VVSR	VVSR
5% NaOH solution	So. Sw. BBlis.	So. Sw. BBlis.	So. Sw. BBlis.	So. Sw. BBlis.	So. Sw. BBlis.	So. Sw. BBlis.
Sward hardness	74	68	62	64	62	58
Flexibility—mandrel	Fl.	Fl.	V Fl.	Fl.	Fl.	Fl.
Adhesion—mandrel	P	P	F	P	P	P
Approximate elongation—mandrel	<3%	<3%	<3%	<3%	<3%	<3%
Gloss	F	F	G	G	G	Ex.
Sanding	G	F	P	F	F	P
Rubbing	G	G	G	G	G	G
Temperature change—cycles	3	3	3	3	5	6
Discoloration	VS	S	Mod.	VS	VS	VS

G	Good
F	Fair
P	Poor
B	Bad
Mod.	Moderate
S	Slight
Dis.	Disintegrated
V	Very
Blis.	Blistered
T	Temporary

CXIV

399	400	401	402	403	404	405	406	407	408	409	410
A synthetic drying oil			Raw castor oil AA			Diamyl phthalate			Dibutyl phthalate		
1	2	3	1	2	3	1	2	3	1	2	3
10	10	10	10	10	10	10	10	10	10	10	10
10	10	10	10	10	10	10	10	10	10	10	10
1	2	3	1	2	3	1	2	3	1	2	3
48	48	48	48	48	48	48	48	48	48	48	48
(7.2)	(7.2)	(7.2)	(7.2)	(7.2)	(7.2)	(7.2)	(7.2)	(7.2)	(7.2)	(7.2)	(7.2)
32	32	32	32	32	32	32	32	32	32	32	32
(4.4)	(4.4)	(4.4)	(4.4)	(4.4)	(4.4)	(4.4)	(4.4)	(4.4)	(4.4)	(4.4)	(4.4)
G	G	G	G	G	G	G	G	G	G	G	G
G	G	F	G	G	G	G	G	G	G	G	G
P	P	P	P	P	P	P	P	P	F	P	P
P	P	P	F	F	F	F	F	P	F	P	P
G	G	G	G	G	G	G	G	G	G	G	G
Br.	Br.	Br.	Br.	Br.	Br.	Br.	Br.	Br.	Br.	Br.	Br.
Br.	Br.	Br.	Br.	F	F	F	F	P	F	F	P
G	F	F	P	P	P	P	P	P	P	P	P
G	G	G	G	G	G	G	G	G	G	G	G
P	P	P	G	F	P	F	F	F	P	F	P
VVSR	SR SBlis.	SR SBlis.	SR	VSR	VSTBl.	OK	OK	OK	OK	VSTBl.	TBl.
OK	VSR	VSR	VSR	OK	OK	VVSR	OK	OK	OK	OK	OK
OK	VSR	SR	VVSR	OK	OK	VVSR	OK	OK	VVSR	OK	OK
So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.
BBlis.	BBlis.	BBlis.	BBlis.	BBlis.	BBlis.	BBlis.	BBlis.	BBlis.	BBlis.	BBlis.	BBlis.
74	79	66	70	58	50	72	62	48	70	54	40
Br.	Br.	Fl.	Br.	Fl.	Fl.	Fl.	Fl.	VFl.	Fl.	VFl.	VFl.
P	P	P	P	P	P	P	P	G	P	G	G
<3%	<3%	<3%	<3%	<3%	<3%	<3%	<3%	>30%	<3%	>30%	>30%
Ex.	Ex.	G	Ex.	Ex.	Ex.	G	G	G	G	Ex.	Ex.
G	F	P	G	F	P	G	F	P	F	P	P
G	G	G	G	G	G	G	G	G	G	G	G
4	4	5	3	4	4	4	4	6	4	6	4
VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS

Bl. Blush
Br. Brittle, breaks in bending
R Rusted
Fl. Flexible
< Less than
> More than
Ex. Excellent
So. Softened
Sw. Swollen

TABLE CXIV

Formula No.	411	412	413	414	415	416
	Diphenyl phthalate			Hydrogenated methyl abietate		
	1	2	3	1	2	3
Ethyl cellulose, lb.	10	10	10	10	10	10
Manila loba A, lb.	10	10	10	10	10	10
Plasticizer, lb.	1	2	3	1	2	3
Butanol, lb.	48	48	48	48	48	48
(gal.)	(7.2)	(7.2)	(7.2)	(7.2)	(7.2)	(7.2)
Xylol, lb.	32	32	32	32	32	32
(gal.)	(4.4)	(4.4)	(4.4)	(4.4)	(4.4)	(4.4)
Adhesion to:						
Steel	G	G	G	G	G	G
Copper	G	G	G	G	G	G
Aluminum	P	F	F	P	F	F
Tin plate	G	F	F	G	G	G
Zinc	G	G	G	G	G	G
Rubber	Br.	Br.	Br.	Br.	Br.	Br.
Cellophane (untreated)	F	F	G	Br.	Br.	Br.
Wood (filled)	G	G	F	F	F	F
Plaster	G	G	G	G	G	G
Glass	G	G	F	F	G	F
Sensitivity to:						
Water	VSR	OK	STBl.	VVSR	VVSR	VVSR VSTBl.
5% NaCl solution	VVSR	OK	OK	OK	VVSR	VVSR
5% HCl solution	OK	OK	OK	VVSR	VVSR	VVSR
5% NaOH solution	So. Sw. BBlis.	So. Sw. BBlis.	So. Sw. BBlis.	So. Sw. BBlis.	So. Sw. BBlis.	So. Sw. BBlis.
Sward hardness	68	64	56	70	66	60
Flexibility—mandrel	Fl.	VFl.	VFl.	Fl.	Fl.	Fl.
Adhesion—mandrel	P	P	F	P	P	P
Approximate elongation—mandrel	<3%	3.2%	4.9%	<3%	<3%	<3%
Gloss	F	F	F	Ex.	Ex.	Ex.
Sanding	G	F	P	G	F	F
Rubbing	G	G	G	G	G	G
Temperature change—cycles	4	6	6	2	2	4
Discoloration	S	Mod.	Mod.	VS	VS	VS

G	Good
F	Fair
P	Poor
B	Bad
Mod.	Moderate
S	Slight
Dis.	Disintegrated
V	Very
Blis.	Blistered
T	Temporary

(Continued)

417	418	419	420	421	422	423	424	425
Ethyl orthobenzoyl benzoate			Tricresyl phosphate			Triphenyl phosphate		
1	2	3	1	2	3	1	2	3
10	10	10	10	10	10	10	10	10
10	10	10	10	10	10	10	10	10
1	2	3	1	2	3	1	2	3
48	48	48	48	48	48	48	48	48
(7.2)	(7.2)	(7.2)	(7.2)	(7.2)	(7.2)	(7.2)	(7.2)	(7.2)
32	32	32	32	32	32	32	32	32
(4.4)	(4.4)	(4.4)	(4.4)	(4.4)	(4.4)	(4.4)	(4.4)	(4.4)
F	G	G	G	G	G	G	G	G
G	G	G	G	G	G	G	G	G
P	P	P	P	P	P	P	F	F
G	G	G	F	F	F	P	P	P
G	G	G	G	G	G	F	F	G
Br.	Br.	Br.	Br.	Br.	Br.	Br.	Br.	Br.
Br.	Br.	Br.	Br.	Br.	Br.	Br.	F	F
P	P	P	G	P	P	F	P	P
G	G	G	G	G	G	G	G	G
G	G	G	G	P	P	G	F	F
SR	SR	STBl.	VSR	VVSR	VSTBl.	VVSR	OK	VSTBl.
VSBlis.	VSBlis.			SBlis.				
VVSR	VSR	OK	OK	OK	OK	OK	OK	OK
OK	OK	OK	VVSR	OK	OK	OK	OK	OK
So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.	So. Sw.
BBlis.	BBlis.	BBlis.	BBlis.	BBlis.	BBlis.	BBlis.	BBlis.	BBlis.
72	64	54	64	64	60	70	60	54
Br.	Br.	Fl.	Fl.	Fl.	Fl.	Br.	Fl.	Fl.
P	P	P	P	P	P	P	P	P
<3%	<3%	<3%	<3%	<3%	<3%	<3%	<3%	<3%
Ex.	Ex.	Ex.	Ex.	Ex.	Ex.	F	P	P
G	G	P	G	F	P	G	F	P
G	G	G	G	G	G	G	G	G
3	4	4	4	4	6	4	4	4
VS	S	S	S	Mod.	Mod.	S	Mod.	B

Bl. Blush
Br. Brittle, breaks on bending
R Rusted
Fl. Flexible
< Less than
> More than
Ex. Excellent
So. Softened
Sw. Swollen

TABLE CXV

RESULTS OF TESTS ON SPIRIT VARNISHES CONTAINING ETHYL CELLULOSE

	Pontianak Varnishes						Manila DBB Varnishes					
Formula No.	426	427	428	429	430	431	432	433	434	435	436	437
Per cent ethyl cellulose	0	5	10	15	20	25	0	5	10	15	20	25
Hardness, Venus pencil No.	2H	3H	4H	4H	4H	5H	2H	3H	3H	4H	4H	5H
Melting range, °C.	143–53	146–56	149–59	151–61	153–63	155–65	120–30	123–33	128–38	132–42	136–46	140–50
Order of moisture resistance	4th	3rd	2nd	1st	1st	1st	4th	3rd	2nd	1st	1st	1st
Cold check resistance, cold cycle on which definite failure occurred	2	3	4	5	11	12	3	4	10	11	>12	>12
Abrasion resistance, grams of sand required to penetrate film of 0.0254-mm. thickness	24	40	1920	5280	8250	9800	60	68	4230	7320	11,416	13,410

In studying the miscibility of cellulose acetobutyrate with the various resins, damar was found to be satisfactory for most purposes. With the solvent composition used in the study of miscibility in films, damar was found to be completely miscible, producing clear films in the proportion of 0.2 part damar and 1 part cellulose acetobutyrate. With 0.7 part damar and 1 part cellulose acetobutyrate, the mixture was found to be partly miscible and the resulting film was cloudy. Miscibility was also determined for damar used in varying proportions with cellulose acetobutyrate and ester plasticizers. With dibutyl phthalate or lindol as the plasticizer, it was found that the mixtures were compatible when containing up to 0.8 part of dewaxed damar.

Experimental evidence indicates that lower amounts of resin and plasticizer should be used with cellulose acetobutyrate than with nitrocellulose. The properties of lacquer films obtained, using the system damar, dibutyl phthalate, cellulose acetobutyrate, were determined and the results obtained are illustrated in Fig. 60.

Tests were conducted on formulations to be used as over-coatings. It was found that cellulose acetobutyrate lacquers would satisfactorily resist exposure on a test fence for a period of one year in Wilmington or five months in Florida. The gloss of the finish was retained until failure. Failure of these lacquers is believed to have been caused by the decomposition of the nitrocellulose enamel underneath.

The solids composition of a damar-containing lacquer which satisfactorily withstood this test is as follows:

Cellulose acetobutyrate, low viscosity	8.0
Damar	0.4
Dibutyl phthalate	3.0

Formula 438 (Table CXVI) is cited as a lacquer used to over-coat automobile enamels. When applied to unpolished nitrocellulose enamel, a good gloss was obtained. Examination at the end of four months showed that a good proportion of the original gloss had been retained. Failure of the panels occurred at the end of seven months.

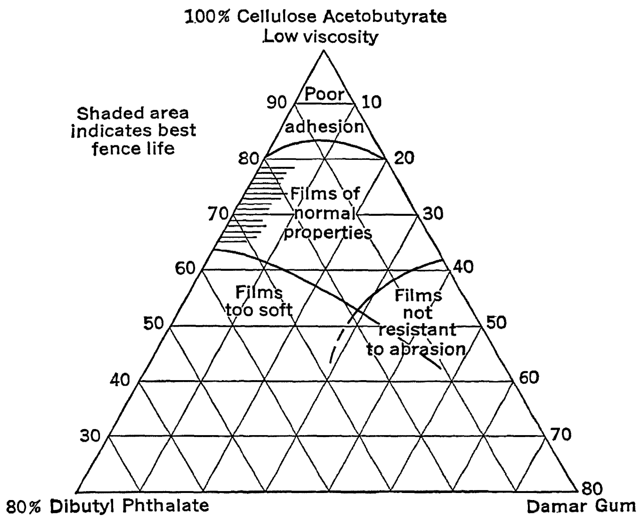


FIG. 60. Properties of lacquer formulae using damar gum, dibutyl phthalate, and cellulose acetobutyrate.

Cellulose acetobutyrate lacquers have been suggested as clear finishes for metal surfaces. Formula 439 is reported as being applied to iron and having resisted exposure for fourteen months.

Development work was also reported on a lacquer for cork tile, it being desired that the resulting product would not be ignited or charred when held for 15 seconds in the flame of a blow torch, which flame was to be held as low as possible. The base formula obtained is given in Table CXVI (formula 440). The lacquer did not ignite and was but slightly charred.

Damar with cellulose acetobutyrate in the formulation of bronzing

TABLE CXVI

DAMAR-CELLULOSE ACETOBUTYRATE LACQUERS

Formula No.	438		439		440		441	
	lb.	gal.	lb.	gal.	lb.	gal.	lb.	gal.
Cellulose acetobutyrate (L.V.)	36	...	12	...	12	...	8	...
Dewaxed damar (dry)	12	...	...	...	4	...	...	...
Dewaxed damar solution	...	...	1*	...	...	...	2†	...
Dibutyl phthalate	12	...	3.5	...	6	...	1	...
Toluol	72	10.0	54.0	7.5	82.3	8.76	...	...
Ethylene dichloride	293	28.2	60.7	5.81	...	...	89	8.53
Butanol	38	5.63	4.1	0.67	...	...	...	...
Butyl acetate	31	4.25	...	...	5.1	0.7	...	...
Cellosolve acetate	38	4.69	...	...	...	...	...	...
Methyl Cellosolve acetate	...	...	13.5	1.61	...	...	...	...
Acetone	...	...	48.0	7.28	82.3	12.48	...	...
Ethyl lactate	...	...	2.7	0.31	10.3	1.24	...	...
Dichlorobutane	...	...	...	...	...	...	20	...

* Containing 45% resin.
† Prepared by dissolving 50 parts of damar in 12.5 parts of toluol and 37.5 parts of denatured alcohol and then permitting the solution to settle.

liquids was reported to be unsatisfactory as certain bronzes caused the formulation to turn green.

Damar was also reported in a sealing lacquer, which was stated to have excellent qualities and to prevent interpenetration between coats of nitrocellulose lacquer (formula 441).

Cellulose Acetopropionate Lacquers. Cellulose acetopropionate, like cellulose acetobutyrate, is a cellulose ester possessing the film characteristics normally attributed to cellulose acetate but having a much broader solubility and miscibility with lacquer ingredients. The material is marketed under the name "Hercose AP." An investigation[17] of the properties of eight pigmented cellulose acetopropionate lacquers containing damar was reported (Table CXVII). The damar solution used is a 50 per cent solution which has been dewaxed.

Cellulose acetopropionate lacquers are suggested in durable, clear metal and cloth finishes, non-fading outdoor enamels, high-gloss over-coated enamel systems, airplane dopes, grease-proof oil-resisting finishes, thermoplastic finishes, and as a pigment-grinding base.

Martin[18] reviewed the properties of the natural resins and their use

[17] "Hercose AP," Hercules Powder Co. booklet, 1940.
[18] R. C. Martin, *Metal Cleaning Finishing,* 5, 159-62 (1933).

TABLE CXVII

COMPOSITION AND PROPERTIES OF PIGMENTED CELLULOSE ACETOPROPIONATE LACQUERS

Formula No.	442	443	444	445	446	447	448	449
Base solution	60	60	60	60	60	60	60	60
Damar solution	6	6	6	6	6	6	6	6
Dibutyl phthalate	4.2	3	4.2	1.8	4.2	3	4.5	3
Maroon paste	11.3	18.7	...	...	...	...	...	...
TiO_2 paste	...	...	12	21	...	...	...	...
Blue paste	...	...	...	...	15	25	...	...
Green paste	...	...	...	...	...	...	7.5	15
Solvent	61.5	55.3	67.8	54.2	97.8	89	72	66
Sward hardness, per cent	...	...	...	...	60	58	...	...
						74 for same formula, RS ½ sec.		
Fence life—failure	Chalked 20 mos.	Chalked 20 mos.	7 mos. Crack and peel	6 mos. Crack and peel	Fade and rust through 15 mos.	6 mos. Crack, blister, rust	Chalking 20 mos.	Chalking 20 mos.
Life of corresponding N/C formula	Chalked, blistered Fade 20 mos.			Bad chalk 12 mos.	...	Blistered 12 mos.	...	Bad chalk 20 mos.

Base Solution	Parts by Weight	Solvent	Parts by Weight
Hercose AP, low viscosity	20	Ethyl acetate	10
Ethyl acetate	8	Butyl acetate	20
Butyl acetate	16	Alcohol	20
Alcohol	16	Butanol	10
Butanol	8	Toluol	40
Toluol	32		

Maroon Paste	Parts by Weight	TiO_2 Paste	Parts by Weight	Blue Paste	Parts by Weight	Green Paste	Parts by Weight
Indian red	25	TiO_2	50	Prussian blue	32	Chrome green	50
Burnt umber	15	Dibutyl phthalate	20	Dibutyl phthalate	12	Dibutyl phthalate	20
Dibutyl phthalate	28	1 : 1 Xylol-butanol	30	Xylol	26	Xylol	15
1 : 1 Xylol-butanol	32			1 : 1 Xylol-butanol	30	Butanol	15

NOTE: All exposures made on clean body steel panels, given 1 coat oil primer (red oxide pigment), baked 1 hr. at 105°C., 3 spray coats enamel, dry overnight, sand, mist coat with solvent, dry, polish.

Chalking on Hercose AP panels not so severe as on nitrocellulose panels.

in nitrocellulose lacquers. Kraus[19] found that in combinations of the various resins and plasticizers exposed to ultraviolet light, the degree of yellowing was not additive but was always greater than the sum of the individual yellowing effects. Especially good light resistance was shown by lacquers containing zellodamar, which is a refined damar. Gardner and Van Heuckeroth[20] made exposure tests on the natural resins by themselves and with solvents, oils, and nitrocellulose. Reference should be made to the original article. Gardner and Faust[21] showed that kauri was a good lacquer addition for outdoor exposure materials. Other work by Gardner[22] indicated the suitability of damar in lacquers for specific applications.

[19] A. Kraus, *Farbe u. Lack,* pp. 206, 221-2 (1930).

[20] H. A. Gardner and A. W. Van Heuckeroth, *Am. Paint and Varnish Mfrs. Assoc., Circ. No. 316,* pp. 447-68 (1927).

[21] H. A. Gardner and J. B. Faust, *Paint Mfrs. Assoc. of U. S., Circ. No. 277,* pp. 83-9 (1926).

[22] H. A. Gardner, *Paint Mfrs. Assoc. of U. S., Circ. No. 252,* pp. 168-73 (1925).

CHAPTER XXI

PAINTS AND ENAMELS

Natural resins are used in the preparation of paints and enamels in the form of both spirit and oil-base varnishes. Such varnishes find application in the formulation of traffic, luminous, concrete, ceiling, wall, furniture, barrel, priming, and fume-proof paints (or enamels).

In formulating natural resin paints it is necessary to avoid the combination of basic pigments with those resins of an acidic nature. All natural resins contain resin acids and esters. With damar, batu, black and pale east india, no trouble is encountered. It is with the manila type resins that care should be taken. A safe rule is always to avoid the incorporation of basic pigments in formulations containing manila resins. In the case of congo and kauri, pigments which are dangerous to use with manilas can sometimes be used by experienced formulators. Compatibility of the resins with basic pigments can be obtained by the use of their non-reactive esterified modifications or by the incorporation of a neutralizing agent such as glycerin during the preparation of the vehicle. Such additions can be made during the running of the resin or the cooking of the varnish.

The reaction between acidic resins and basic pigments is not a complete disadvantage, for skillful formulators may combine the two components in the correct proportions to obtain a desired degree of false body. The reactivity of a number of typical oil varnishes has already been tabulated in the chapter on physical and chemical properties.

Strictly speaking, any pigmented non-cellulosic surface coating containing a resin can lay claim to the name of enamel. However, in this chapter the authors have restricted this term to those resin-containing compositions which dry to a glossy film. These may be prepared from either spirit- or oil-base resin vehicles. Numerous examples of such vehicles are to be found throughout the chapters devoted to oil and spirit varnishes. For those compositions where gloss may be only an incidental property, the word paint has been applied despite their resinous base.

Traffic Paints. Known variously as center-line, striping, road-marking, highway-marking, and zone paints or lacquers, traffic paints are

demanded to dry rapidly with the formation of hard films which do not "pick up" in traffic and which resist abrasion by the wheels of vehicles. In addition, they are expected to withstand a wide range of temperature, climate, and weather, even in one locality. The useful life of a traffic paint is also dependent upon the type of road surface to which it is applied.

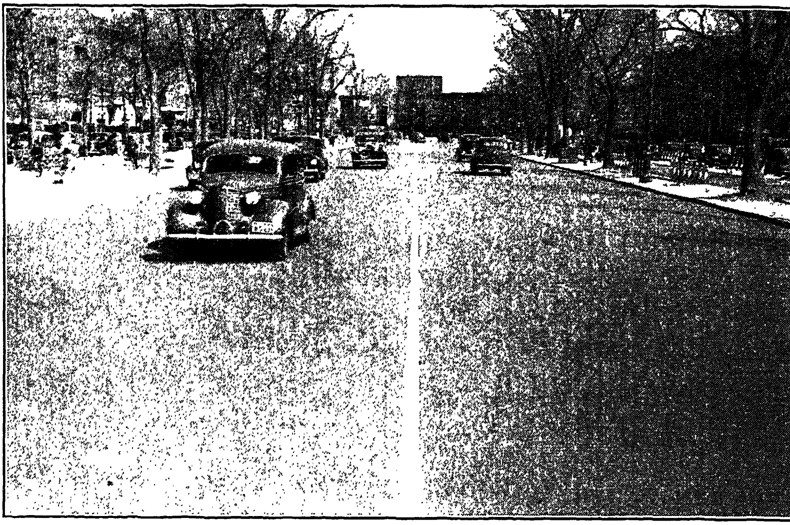


FIG. 61. A traffic stripe in use.

The constituents of traffic paints must be as inexpensive as possible, and, consistent with cost, must give satisfactory service. Natural resins, because of their own low cost and their solubility in cheap solvents, are eminently fitted for such use and have found wide acceptance in this field.

A number of investigators have studied pigmentation and testing.[1] Investigative work has been performed by pigment manufacturers, the National Bureau of Standards, state highway departments, or large paint manufacturers.

Almost all states have specifications for traffic paints. Many states

[1] H. A. Nelson and S. Werthan, *Ind. Eng. Chem.*, **18**, No. 9, 965 (1926).

Sweat, *Paper No. 19,* Maine Technology Experiment Station, Univ. of Maine.

E. F. Hickson, *Circ. No. 532,* Sci. Section of American Paint and Varnish Manufacturers Association (April, 1937).

E. M. Rogers, *Am. Paint J.*, May 16, 1938.

L. Shuger, *Drugs, Oils & Paints,* October, 1939; *ibid.*, December, 1939; *Paint Industry Mag.*, January, 1940.

specify that the paint shall be mixed at the factory ready for application through spray machines without the addition of thinner. Specifications for white traffic paints often call for the addition of a blue pigment paste to overcome any yellow tint, and the addition to the finished paint (spirit paints only) of 1 per cent by volume of amyl acetate as an aid to ease of application.

The properties desirable in a traffic paint can be summarized as follows:

1. Low cost.
2. Rapid drying.
3. Resistance to abrasion (hardness).
4. Resistance to "pickup."
5. Minimum solvent action on road material (bleeding).
6. Good adhesion to road material.
7. Good visibility (day and night).
8. Good weathering resistance.
9. Good color and color retention.
10. Resistance to the particular local climate or rapid changes therein.
11. Ease of application (suitable consistency).
12. Stability in container.
13. Minimum coverage at maximum hiding.

These properties cannot always be secured in one paint. Frequently one will be obtained only at the expense of another. For this reason, an ideal traffic paint would be one that has been "custom made" for a particular job at a particular location. In this way, properties not essential to a specific use can be disregarded, to the betterment of the important considerations.

For example, a paint designed for use on a heavily traveled road presents a hard surface when dry, but usually lacks the necessary flexibility to make it suitable for use on a rural road where the ultimate failure is by weathering rather than by abrasion. Conversely, a paint designed for the latter use would usually not have sufficient hardness to withstand the abrading action encountered on a heavily traveled highway.

Traffic paints are generally formulated to dry to a flat or semi-gloss finish. In order to avoid the loss of night visibility, gloss paints are not used. The degree of flatness can be controlled by the choice of pigments and inerts, their particle size in the finished paint, the use of flatting agents, and the ratio of pigment to binder. Nelson and Werthan[2] determined through the examination of paints of satisfac-

[2] N. A. Nelson and S. Werthan, *Ind. Eng. Chem.*, **18**, 965 (1926).

tory night visibility that this property is due to coarse inert pigment in the paint.

To obtain a paint with good color, brightness, and opacity, good pigment suspension, proper consistency for application, and reasonable resistance to abrasion, that coarse inert should be chosen which can be used in the smallest proportions and still obtain a paint with satisfactory visibility. Considering all the properties of the paint, several investigators have found that satisfactory results can be obtained with an inert of fibrous talc or asbestine. Ground glass is sometimes enlisted as an aid to night visibility, either by dusting the wet stripe with it or by adding it to the paint.

The resin used does not affect the gloss to any great extent, except the East India class of resins (batu, black east india, and pale east india). When these resins are used, a slightly flatter finish can be obtained but the difference is not great enough to warrant their recommendation solely on the basis of this property.

Traffic paints appear in several colors: white, yellow (or yellow-orange), red, and black. White is the most widely used because of its superior night visibility. Colored paints, besides showing a greater tendency to discolor, suffer the drawback of possessing lower night visibility.

The pigments generally used are lithopone, titanium-base materials, and zinc oxide, with additions of various inerts to increase resistance to wear and to improve visibility. In paints other than white, pigments such as chrome yellow and related lead chromates, molybdate and organic reds, carbon black, and iron oxides are used. Lithopone, despite its proved inferiority to titanium-base pigments, continues to be specified by many states.

Traffic paint vehicles may be summed up, as far as natural resin applications are concerned, as being either cold-cut, quick-drying spirit varnishes, or else rapidly drying oil varnishes. In the former field, natural resins receive negligible competition from synthetic resins, whereas in the latter, both types are used. The spirit-varnish type dry by evaporation of the solvent, whereas the oil base dry by oxidation of oil and evaporation of thinner. A spirit traffic paint will dry to the touch in 15 to 20 minutes and can bear traffic within 45 to 60 minutes.

In Table CXVIII there is a collection of thirty-nine traffic paint formulae from some twenty-six states of the Union. These formulae include both oil and spirit vehicles. In the collection, it is to be noted that one particular formulation has been adopted in toto, or with slight

change in pigmentation, by fourteen states. This formula, known as the California formula, was developed by the California State Highway Department in 1932 and was the pioneering formula in the quick-drying spirit-base traffic paint field. Since that time, other specifications have appeared for spirit-base traffic paints, but the change was always in the pigmentation and not in the vehicle.

The vehicle of the California formula remains the most widely used for quick-drying traffic paints (Table CXVIII).

The vehicle is prepared by simple cold cutting, i.e., the resin is dissolved in the solvent without the use of heat. After solution the small amount of insoluble matter is removed by filtering or settling. Sufficient resin must be used so that the clarified solution meets the specified 35 per cent resin content. If the original insoluble content be known, it is a simple matter to calculate the exact amount of resin to use.

When grinding the pigments with the vehicle, it is desirable to use a ball or pebble mill, as the high volatility of the solvent precludes the grinding of the paste on an open mill such as the roller or buhrstone mills.

The authors have published[3] the results of a study of natural resins in traffic paints. The prime concern in such an investigation was the improvement of traffic paint vehicles, with a secondary interest in their pigmentation.

The pigment composition of the paints was maintained constant (with the exception of one series), and changes were made within the vehicle. Moreover, each change had to be made while keeping the remaining components of the vehicle constant.

Taking the California vehicle as a starting point, changes were made in resin, oil, the ratio of resin to oil, the ratio of pigment to binder in the dry film, the addition of elemi to improve adhesion and, to a small degree, the volatility of the solvents. With such a number of possible variables, the project resolved itself into the preparation of several series of paints. Each series had one vehicle component as a variable with the others remaining unchanged. A different vehicle component was varied in each series. In this manner each component was isolated in turn and the effect of the change was observed.

The aim of each series is given in the summary of formulations. All percentages are by weight.

Series A. The California traffic paint formula was made with differ-

[3] C. W. Kopf and C. L. Mantell, *Paint, Oil Chem. Rev.*, No. 11, 7; No. 12, 44; No. 14, 9 (1940).

TABLE CXVIII

Traffic Paint Formulations

	Formula No.	450	451	452	453	454	455	456	457	458	459	460	461	462
		Alabama		Arizona	Arkansas	Calif.	Colorado		Idaho	Illinois	Indiana		Kansas	
		White pavement center stripe	Yellow pavement center stripe	White traffic line lacquer	White traffic stripe	White traffic line lacquer	Orange traffic spirit paint	White traffic spirit paint	Yellow traffic line lacquer	White zone marking paint	White traffic paint	Yellow traffic paint	White traffic line marking paint	Persian red traffic paint
1	Gum vehicle percentage on basis of finished paint	58–55	58–55	58–55	40–35	58–55	70	58–55	73–70	58–55	38–35	50–45	58–55	68–63
2	Pigment, on basis of finished paint	42–45	42–45	42–45	60–65	42–45	30	42–45	27–30	42–45	62–65	50–55	42–45	32–37
3	Per cent volatile matter on basis of finished paint	35–38	35–38	35–38		35–38	44–46	35–38	44–47	35–38			35–38	35–38
4	Per cent non-volatile matter on basis of finished paint	65–62	65–62	65–62		65–62	56–54	65–62	56–53	65–62			65–62	65–62
	Constitution of pigment, percentage of total pigment													
5	Cadmium red													63% min.(2)
6	Lead chromate													63% min.(3)
7	Chrome yellow		60–70				70		100			55–60		
8	Lithopone				68–70						67–71			
9	Siliceous material				32–30						33–29	45–40		
10	Titanium-barium pigment	100	40–30	100		100	20	100		100			100	
11	Asbestine						10							37% max.(4)
12	Zinc oxide													
13	Normal lead chromate													
	Constitution of gum vehicle on basis of 100 parts by weight													
14	Manila DBB	35–37	35–37	35–37		35–37	35–37	35–37	35–37	35–37			35–37	35–37
15	Gum varnish				X						40% min.	40% min.		
16	East india batu													
17	Solvent as given below	65–63	65–63	65–63		65–63	65–63	65–63	65–63	65–63			65–63	65–63
	Constitution of solvent on basis of 100 parts by volume													
18	Raw tung oil	15	15	15		15	15	15	15	10–12 by wt.			15(1)	15(1)
19	Normal butyl alcohol	17	17	17		17	17	17	17	10–12 " "			17	17
20	Acetone	34	34	34		34	34	34	34	20–22 " "			34	34
21	Denatured alcohol #1	34	34	34		34	34	34	34	20–22 " "			34	34
22	Amyl acetate													
	Constitution of thinner on basis of 100 parts by volume													
23	Turpentine													
24	Mineral spirits													
25	Normal butyl alcohol						20	20	20					
26	Acetone			33		33	40	40	40					
27	Denatured alcohol #1			67		67	40	40	40					
	Add to 500 gal. of product													
28	Amyl acetate, gallons	5	5	5		5	5	5						
	To remove yellow tint:													
29	Prussian blue in oil	X		X		X		X					X	
30	Ultramarine blue paste													

1 "Cicoil" (oiticica oil) permitted as a substitute for tung oil.
2 And/or lead chromate.
3 And/or cadmium red.
4 And/or china clay.
5 Diatomaceous silica.
6 Titanium-magnesium-barium pigment.
7 Not specified. Total non-volatile matter must not be less than 25 per cent by weight.
8 A nitrocellulose lacquer of unspecified composition is used.
9 TiO_2 may be added to match specified shade.
10 Not specified. Vehicle must be non-yellowing.
11 Or titanium-barium pigment.
12 Or lithopone.
13 Vermont also uses a white traffic lacquer similar to that of New Hampshire with the total non-volatile content specified to be not less than 40 per cent by weight.
14 Not specified.

TABLE CXVIII (*Continued*)

	Formula No.	463	464	465	466	467	468	469	470	471	472	473	474	475
		Kentucky	Michigan	Mississippi		Missouri	Montana		Nevada	New Hampshire	New York	North Carolina	North Dakota	Oklahoma
		White "M"	White pavement marking paint	White traffic zone paint	Yellow center line stripe	White center line paint	White traffic paint heavy duty	Yellow traffic paint	White	Yellow traffic lacquer	White traffic zone paint	White	Yellow	White traffic line lacquer
1	Gum vehicle percentage on basis of finished paint	58–55	58–55	36–34	50–40	58–55	58–55	58–55	58–55	[7]	40–35	42–38	62–58	58–55
2	Pigment, on basis of finished paint	42–45	42–45	64–66	50–60	42–45	42–45	42–45	42–45	[7]	60–65	58–62	38–42	42–45
3	Per cent volatile matter on basis of finished paint	35–38	35–38			35–38	35–38	35–38	35–38		20–22.5			35–38
4	Per cent non-volatile matter on basis of finished paint	65–62	65–62			65–62	65–62	65–62	65–62		80–77.5			65–62
	Constitution of pigment, percentage of total pigment													
5	Cadmium Red													
6	Lead chromate													
7	Chrome yellow				35–60			100		100			100[9]	
8	Lithopone				0–25						60% min.	54–58		
9	Siliceous material			19–21[5]	20–40 inerts						20% min.			
10	Titanium-barium pigment	100	100	55–57		100	100		100[6]					100
11	Asbestine													
12	Zinc oxide			23–26							20% max.	42–48		
13	Normal lead chromate													
	Constitution of gum vehicle on basis of 100 parts by weight													
14	Manila DBB	35–37	35–37			35–37	35–37	35–37	35–37	[8]			[10]	35–37
15	Gum varnish			40% min.							50% min.	37% min.		
16	East india batu													
17	Solvent as given below	65–63	65–63			65–63	65–63	65–63	65–63					65–63
	Constitution of solvent on basis of 100 parts by volume													
18	Raw tung oil	15	17			15	15	15	15					15
19	Normal butyl alcohol	17	17			17	17	17	17					17
20	Acetone	34	32			34	34	34	34					34
21	Denatured alcohol #1	34	34			34	34	34	34					34
22	Amyl acetate													
	Constitution of thinner on basis of 100 parts by volume													
23	Turpentine													
24	Mineral spirits													
25	Normal butyl alcohol													
26	Acetone													
27	Denatured alcohol #1													
	Add to 500 gal. of product													
28	Amyl acetate, gallons		5				5							5
	To remove yellow tint:													
29	Prussian blue in oil					X	X							X
30	Ultramarine blue paste		X											

[1] "Cicoil" (oiticica oil) permitted as a substitute for tung oil.
[2] And/or lead chromate.
[3] And/or cadmium red.
[4] And/or china clay.
[5] Diatomaceous silica.
[6] Titanium-magnesium-barium pigment.
[7] Not specified. Total non-volatile matter must not be less than 25 per cent by weight.
[8] A nitrocellulose lacquer of unspecified composition is used.
[9] TiO_2 may be added to match specified shade.
[10] Not specified. Vehicle must be non-yellowing.
[11] Or titanium-barium pigment.
[12] Or lithopone.
[13] Vermont also uses a white traffic lacquer similar to that of New Hampshire with the total non-volatile content specified to be not less than 40 per cent by weight.
[14] Not specified.

TABLE CXVIII (*Continued*)

	Formula No.	476	477	478	479	480	481	482	483	484	485	486	487	488
		Oregon		Pennsylvania			Vermont	Washington					Wisconsin	Wyoming
		Yellow traffic line lacquer No. 1	White traffic line lacquer No. 2	Yellow zone traffic paint spec. P-91	Yellow zone traffic paint spec. P-92	White 13-C for concrete and brick	White(13)	Light yellow traffic paint "G-6"	Medium yellow traffic paint "G-7"	White traffic paint "G-8"	Yellow traffic paint "G-9"	White traffic paint "G-10"	Yellow traffic paint	Center traffic line paint
1	Gum vehicle percentage on basis of finished paint	73–70	58–50	40–35	35–33	40–33	(14)	70	70	58	70	62	41–38	73–70
2	Pigment, on basis of finished paint	27–30	42–45	60–65	65–67	60–67	(14)	30	30	42	30	38	59–62	27–30
3	Per cent volatile matter on basis of finished paint	44–47	35–38		20–21		(14)	37.6	37.6	31.2	37.8	35.2		44–47
4	Per cent non-volatile matter on basis of finished paint	56–53	65–62		80–79		(14)	62.4	62.4	68.8	62.2	64.8		56–53
	Constitution of pigment, percentage of total pigment													
5	Cadmium red						(14)							
6	Lead chromate													
7	Chrome yellow	100						40	35		35		31–33	100
8	Lithopone			45–50	30–33	45% min.(11)		60	65				59–60	
9	Siliceous material			30–20	32–30	30–32 inerts							9–11	
10	Titanium-barium pigment		100			45% min.(12)				100	59	94		
11	Asbestine										6	6		
12	Zinc oxide				10–12	10–25								
13	Normal lead chromate			23–28	28–23									
	Constitution of gum vehicle on basis of 100 parts by weight													
14	Manila DBB	35–37	35–3					34.7	34.7	34.7	34.5	32.4		35–37
15	Gum varnish			X		40% min.	X				11.5 raw tung oil	10.8 raw tung oil	40% min.	
16	East india batu													
17	Solvent as given below	65–63	65–63		60 max.			65.3	65.3	65.3	54	56.8		65–63
	Constitution of solvent on basis of 100 parts by volume													
18	Raw tung oil	15	15					17.6	17.6	17.6				15
19	Normal butyl alcohol	17	17					16.4	16.4	16.4	19.8	18.8		17
20	Acetone	34	34					32.2	32.2	32.2	39.1	39.7		34
21	Denatured alcohol #1	34	34					32.4	32.4	32.4	39.4	40.1		34
22	Amyl acetate							1.3	1.3	1.3	1.6	1.4		
	Constitution of thinner on basis of 100 parts by volume													
23	Turpentine													
24	Mineral spirits													
25	Normal butyl alcohol	20						20	20	20				
26	Acetone	40						40	40	40				
27	Denatured alcohol #1	40						40	40	40				
	Add to 500 gal. of product													
28	Amyl acetate, gallons													
	To remove yellow tint:													
29	Prussian blue in oil		X											
30	Ultramarine blue paste													

1 "Cicoil" (oiticica oil), permitted as a substitute for tung oil.
2 And/or lead chromate.
3 And/or cadmium red.
4 And/or china clay.
5 Diatomaceous silica.
6 Titanium-magnesium-barium pigment.
7 Not specified. Total non-volatile matter must not be less than 25 per cent by weight.
8 A nitrocellulose lacquer of unspecified composition is used.
9 TiO_2 may be added to match specified shade.
10 Not specified. Vehicle must be non-yellowing.
11 Or titanium-barium pigment.
12 Or lithopone.
13 Vermont also uses a white traffic lacquer similar to that of New Hampshire with the total non-volatile content specified to be not less than 40 per cent by weight.
14 Not specified.

ent resins. This was done to obtain the effect of the hardness of the resin on the durability of the paint.

The California formula calls for a straight titanium-barium pigmentation. For the test paints (with the exception of numbers S-1, H-5, H-6, H-7, and H-8) a combination of 63 per cent titanium-barium pigment (30 per cent TiO_2) and 37 per cent asbestine was chosen. The formula covers all the paints in this series: 55 per cent resin vehicle (35 per cent resin; 65 per cent solvent made as follows: 15 raw tung oil (parts by volume), 17 butanol, 34 acetone, 34 ethyl alcohol); 45 per cent pigment (63 per cent titanium-barium pigment, 37 per cent asbestine).

The resins were: A-2, manila DBB; A-3, manila loba; A-4, manila MA; A-6, congo dust (cold cut).

Although the softer resins lack good abrasion resistance, they were included because their very softness might make them preferable for traffic paints on rural highways where films of more flexibility are required and where abrasion resistance is of secondary importance. Congo dust dissolved satisfactorily in the vehicle of the California formula.

Series B. Series B was similar to Series A in that the resin was the variable, the resins being: B-1, batu; B-2, black east india; B-3, pale east india; B-4, run congo.

However, these resins are insoluble in the California solvent and instead require coal-tar or petroleum solvents. The solvent was 15, raw tung oil (parts by volume); 10, xylol; 35, toluol; 40, benzol. Aside from the solvent and resin changes, the formula for Series B was a duplicate of that in Series A.

Series C. In this series, changes were made in the solvent of the California formula. Acetone was eliminated and replaced with less volatile solvents in an attempt to discover the effect, if any, of the drying rate on film durability. Durability might be sacrificed when a paint film is deposited from such a quick-drying vehicle as is called for in the California formula.

Only two paints were made for Series C. With the exception of their solvent combinations they were duplicates of A-2 (manila DBB). The altered solvent combinations follow (parts by volume): C-1–15 raw tung oil, 17 butanol, 68 ethyl alcohol; C-12–15 raw tung oil, 34 butanol, 51 ethyl alcohol.

Series E. In Series E, other oils were substituted for the high-priced tung oil specified in the California formula. The tung oil present in the California traffic paint acts mainly as a plasticizer (being only 6.1

per cent by weight of the finished paint) and it was believed that other oils, notwithstanding their inferior drying rate, durability, and color retention, could be used with a saving in price and no reduction in quality.

In this series, therefore, all factors were kept constant save the oil. In all the resin was manila DBB; the formula corresponded to that of Series A except for the substitution of the following oils: E-1, kettle-bodied linseed oil; E-2, blown soybean oil; E-3, bodied perilla oil; E-4, oiticica oil; E-5, processed fish oil; E-6, dehydrated castor oil; E-7, blown castor oil.

Series F. In order to determine whether adhesion and flexibility could be improved by the addition of elemi, three paints were prepared containing different amounts of it. Too much elemi had to be avoided, for an excessive amount will produce an undesirable after-tack with its attendant pickup. Such a paint would become dirty very quickly.

Additions of elemi were made to the standard California vehicle (manila DBB) as follows: F-1, 2 per cent of elemi added to California vehicle; F-2, 6 per cent of elemi added to California vehicle; F-3, 10 per cent of elemi added to California vehicle. Such amounts of elemi dissolve satisfactorily in the solvents of the California formula. Using these vehicles, traffic paints were prepared following the formula of Series A.

Series H. It was hoped to determine the importance of the pigment-volume to binder-volume ratio in traffic paint films. Paints with pigment volumes of 28 per cent, 34 per cent, 40 per cent, and 46 per cent were made. For each of these pigment volumes, two paints were made using different pigmentations, one containing 63 per cent titanium-barium pigment and 37 per cent asbestine, and the other containing 63 per cent titanium-calcium pigment and 37 per cent asbestine.

Manila DBB was used as the resin and the ratio of DBB to tung oil was kept constant at 3 to 1. The solids content of all eight paints was set at 70 per cent.

Series J. This series concerned itself with the effect of changing the oil-to-resin ratio. With manila DBB as the resin and raw tung oil as the oil, five paints were prepared using the following vehicles (percentages by weight):

	J-1	J-2	J-3	J-4	J-5
Raw tung oil	0	5	10	15	20
Manila DBB	50	45	40	35	30
Solvent as given below	50	50	50	50	50

TABLE CXIX

Traffic Paint Formulations

Formula No.	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505
Traffic Paint No.	A-2	A-3	A-4	A-6	B-1	B-2	B-3	B-4	C-1	C-2	E-1	E-2	E-3	E-4	E-5	E-6	E-7
Variable	Resin				Resin				B.P. of solvent		Oil						
% Resin vehicle	55	55	55	55	55	55	55	55	55	55	55	55	55	55	55	55	55
% Pigment	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45
Composition of resin vehicle																	
Resin	DBB	Loba	MA	Congo dust	Batu	Black E.I.	Pale E.I.	Run congo	DBB	DBB	DBB	DBB	DBB	DBB	DBB	DBB	DBB
Oil	Tung	Tung	Tung	Tung	Tung	Tung	Tung	Tung	Tung	Tung	Lin-seed	Soy-bean	Perilla	Oiticica	Fish	Dehy. castor	Castor
% Resin	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35
% Oil																	
% Solvent	"65"	"65"	"65"	"65"	"65"	"65"	"65"	"65"	"65"	"65"	"65"	"65"	"65"	"65"	"65"	"65"	"65"
Composition of solvent (in parts by vol.)																	
Oil	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Butanol	17	17	17	17		10 Xylol			17	34	17	17	17	17	17	17	17
Acetone	34	34	34	34		40 Benzol			None	None	34	34	34	34	34	34	34
Denatured alcohol	34	34	34	34		35 Toluol			68	51	34	34	34	34	34	34	34
Composition of pigment																	
% Titanium-barium pigment (30% TiO_2)	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63
% Asbestine FT	37	37	37	37	37	37	37	37	37	37	37	37	37	37	37	37	37
% Volatile matter	29.7	29.7	29.7	29.7	30.1	30.1	30.1	30.1	29.8	29.8	29.6	29.8	29.7	29.5	29.5	29.5	29.5
% Non-volatile matter	70.3	70.3	70.3	70.3	69.9	69.9	69.9	69.9	70.2	70.2	70.4	70.2	70.3	70.5	70.5	70.5	70.5
% Resin	19.2	19.2	19.2	19.2	19.2	19.2	19.2	19.2	19.2	19.2	19.2	19.2	19.2	19.2	19.2	19.2	19.2
% Oil	6.1	6.1	6.1	6.1	5.7	5.7	5.7	5.7	6.0	6.0	6.2	6.0	6.1	6.3	6.3	6.3	6.3
% Solvent	29.7	29.7	29.7	29.7	30.1	30.1	30.1	30.1	29.8	29.8	29.6	29.8	29.7	29.5	29.5	29.5	29.5
% Pigment	45.0	45.0	45.0	45.0	45.0	45.0	45.0	45.0	45.0	45.0	45.0	45.0	45.0	45.0	45.0	45.0	45.0
% Resin volume (in dried paint film)	43.0	43.0	43.0	43.0	43.4	43.4	43.4	43.4	43.1	43.1	43.2	43.2	43.0	43.2	43.2	43.2	43.2
% Oil volume " " " "	19.5	19.5	19.5	19.5	18.7	18.7	18.7	18.7	19.3	19.3	19.6	19.6	19.5	19.5	19.5	19.5	19.5
% Pigment volume " " " "	37.5	37.5	37.5	37.5	37.9	37.9	37.9	37.9	37.6	37.6	37.3	37.3	37.5	37.3	37.3	37.3	37.3
Weight—lb./gal.	11.56	11.47	11.42	11.44	11.63	11.77	11.87	11.72	11.46	11.47	11.49	11.98	11.47	11.43	11.96	11.49	11.53
Mobility—secs. (Gardner 100-g. 51-hole disk)	7.2	12.5	7.4	22.4	35.1	20.6	14.3	4.9	14.6	17.5	9.3	10.4	7.6	11.0	13.1	7.5	8.8

TABLE CXIX (*Continued*)

Formula No.	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522
Traffic Paint No.	F-1	F-2	F-3	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8	J-1	J-2	J-3	J-4	J-5	S-1
Variable	2, 6, 10% Add'ns. of elemi to vehicle			Pigment volume								Oil-to-resin ratio					None
% Resin vehicle	55	55	55	62.2	57.4	53.3	49.6	65.4	60.5	56.2	52.3	55	55	55	55	55	55
% Pigment	45	45	45	37.8	42.6	46.7	50.4	34.6	39.5	43.8	47.7	45	45	45	45	45	45
Composition of resin vehicle																	
Resin	DBB plus elemi			DBB	DBB	DBB	DBB	DBB	DBB	DBB	DBB	DBB	DBB	DBB	DBB	DBB	DBB
Oil	Tung	Tung	Tung	Tung	Tung	Tung	Tung	Tung	Tung	Tung	Tung	Tung	Tung	Tung	Tung	Tung	Tung
% Resin	36.3	38.7	40.9	38.8	35.8	32.8	29.6	40.6	37.9	34.9	32.0	50	45	40	35	30	35
% Oil				12.9	11.9	10.9	9.9	13.5	12.6	11.7	10.7	0	5	10	15	20	
% solvent	"63.7"	"61.3"	"59.1"	48.3	52.3	56.3	60.5	45.9	49.5	53.4	57.3	50	50	50	50	50	"65"
Composition of solvent (in parts by vol.)																	
Oil	15	15	15														15
Butanol	17	17	17	20	20	20	20	20	20	20	20	20	20	20	20	20	17
Acetone	34	34	34	40	40	40	40	40	40	40	40	40	40	40	40	40	34
Denatured alcohol	34	34	34	40	40	40	40	40	40	40	40	40	40	40	40	40	34
Composition of pigment																	
% Titanium-barium pigment (25% TiO_2)																	100
% Titanium-barium pigment (30% TiO_2)	63	63	63	63	63	63	63					63	63	63	63	63	
% Titanium-calcium pigment (30% TiO_2)								63	63	63	63						
% Asbestine FT	37	37	37	37	37	37	37	37	37	37	37	37	37	37	37	37	
% Volatile matter	29.0	27.9	27.0	30	30	30	30	30	30	30	30	27.5	27.5	27.5	27.5	27.5	29.7
% Non-volatile matter	71.0	72.1	73.0	70	70	70	70	70	70	70	70	72.5	72.5	72.5	72.5	72.5	70.3
% Resin	20.0	21.3	22.5	24.2	20.6	17.5	14.7	26.5	22.9	19.6	16.7	27.5	24.8	22.0	19.2	16.5	19.2
% Oil	6.0	5.8	5.5	8.0	6.8	5.8	4.9	8.9	7.6	6.6	5.6	None	2.7	5.5	8.3	11.0	6.1
% Solvent	29.0	27.9	27.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0	27.5	27.5	27.5	27.5	27.5	29.7
% Pigment	45.0	45.0	45.0	37.8	42.6	46.7	50.4	34.0	39.5	43.8	47.7	45.0	45.0	45.0	45.0	45.0	45.0
% Resin volume (in dried paint film)	44.4	46.2	48.0	49.0	45.0	40.8	36.7	48.7	44.9	40.6	36.6	62.4	54.9	47.4	40.4	33.9	45.6
% Oil volume " " " "	18.8	17.8	16.6	23.0	21.0	19.2	17.3	23.3	21.1	19.4	17.4	0.0	8.4	16.8	24.7	32.0	20.8
% Pigment volume " " " "	36.8	36.0	35.4	28.0	34.0	40.0	46.0	28.0	34.0	40.0	46.0	37.6	36.7	35.8	34.9	34.1	33.6
Weight—lb./gal.	11.51	11.59	11.60	10.70	11.17	12.02	12.46	10.28	10.64	10.23	11.36	11.75	11.69	11.56	11.58	11.40	11.67
Mobility—secs. (Gardner 100-g. 51-hole disk)	9.4	11.0	13.0	8.1	7.8	6.7	5.9	12.7	10.1	6.0	7.3	26.6	21.4	14.7	9.9	8.6	4.5

NOTE: Unless otherwise stated, all percentages are weight percentages and are based on the finished paint.
Wherever the figures for "% Solvent" are given within quotation marks it indicates that oil, as well as solvent, is included in this figure.

The composition of the solvent shown in the table is given below in the general formula for paints of this series.

55 per cent resin vehicle
  ( ) per cent manila DBB
  ( ) per cent raw tung oil
  50 per cent solvent made as follows:
    20 butanol (parts by volume)
    40 acetone
    40 ethyl alcohol
45 per cent pigment
  63 per cent titanium-barium pigment
  37 per cent asbestine

Series S. For purposes of comparison, S-1 has been prepared following the California formula as given previously.

All the paints were ground in a pebble mill as 60 per cent pigment pastes. To the finished paints an organic blue ground in oil and 1 per cent by volume of amyl acetate were added. Complete formulations are given in Table CXIX.

The table is divided into two parts, the first covering the formulation data and the second listing calculated percentages and laboratory test results.

Some explanation is needed concerning several items in this table. The term "solvent" as used in state specifications refers to a combination of true solvents and oil. As Table CXIX also lists the percentage of true solvent, it was necessary to insert quotation marks whenever "solvent" was used in the former sense (oil + solvents). Under the heading "Constitution of Resin Vehicle," the percentages of oil and solvent are given separately for series H and J, but for all the other series the oil and true solvent contents are given together as "per cent solvent."

In practice traffic paints usually are applied by spraying or by means of a roller arrangement of one of a number of designs. For the application of the paints in this investigation, a small-sized model of one of the latter type was used (see Fig. 62).

Essentially, it consisted of a sled 6 in. wide, with a roller composed of individual metal washers across one end. The washers were about ⅛ in. thick and were closely arranged on a shaft with no binding between adjacent washers. The shaft diameter was only about one-half that of the washer hole, thus permitting a washer, or group of washers, to rise without breaking the road contact of the remaining washers should any unevenness of road surface be encountered by the

roller. Tangent to the washers' circumference at the point of road contact and at an angle of 30 degrees, there was a solid row of rectangular metal bars down which the paint flowed to be spread by the washers. The sled was drawn by a chain and guided by a rigid handle. Films of fairly uniform thickness can be obtained by this unit.

FIG. 62. Application of a traffic paint test strip.

The use of a frame of wooden two-by-fours as a guide proved to be an aid to the application of the paints. With such an arrangement, test stripes were put down very quickly and accurately. The test stripes were applied in 10-ft. lengths transversely across the road rather than longitudinally. In this manner each stripe suffered equal abuse. The 10-ft. length was marked off on the wooden frame.

The paint was fed to the applicator from a veterinary's syringe which previously had been calibrated in fluid ounces. In this manner the quantity of paint applied was known and the gallons-per-mile consumption could be calculated.

All paints were applied to the road without thinning at a constant rate of 25 gal. per mile of 6-in. stripe. Usually in testing traffic paints on the road, all the finished paints are thinned to the same consistency. All these paints, although not of the same consistency, were

in a range suitable for use with the type of applicator described. This was fortunate, for thinning would have meant the application of films containing unequal amounts of "actual paint as formulated" with the result that this added variable would have acted to obscure the effects of the very variables under study.

The choice of an application rate for traffic paints is determined by the character of the paint, including consistency and hiding power,

FIG. 63. Testing of traffic paints on a Long Island road.

the type and form of road surface, and the method of application. The form of road surface particularly affects the mileage of a traffic paint. For a 6-in. stripe of a given paint this consumption may range from 15 gal. per mile for a very smooth road, to 50 gal. per mile for a rough concrete road of the type that has been raked just before setting.

The paints were applied in October, to a fairly smooth concrete highway in Nassau County, Long Island (Fig. 63). The road had two lanes, one for each direction, and was used by an estimated 800 to 1,000 cars daily. The test stripes were inspected every four weeks and observations were made of their durability, points of failure (whether distributed or confined to areas at the point of tire contact), color,

and general appearance. All observations were performed visually without the use of instruments. Attempts have been made by previous investigators to use instruments, but these invariably were discarded in favor of the naked eye.

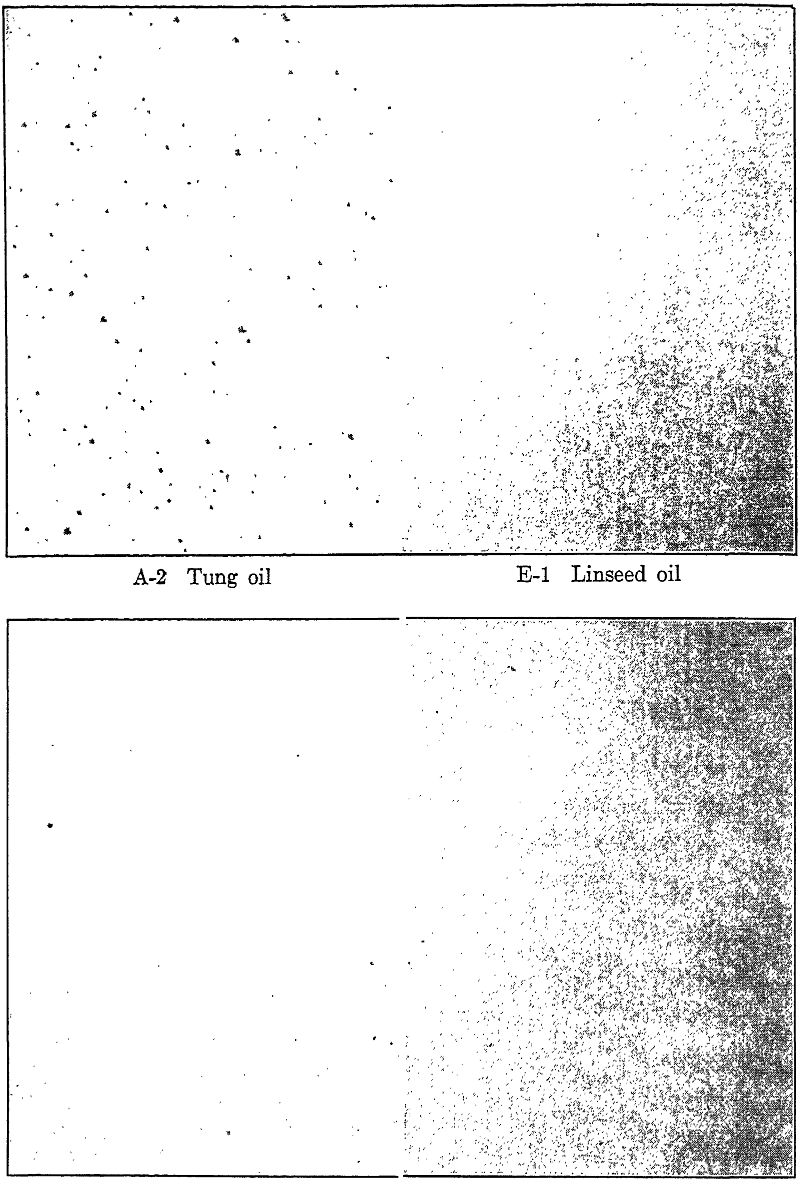
As a supplementary test, stripes were also put down on an asphalt road along the Brooklyn waterfront (Fig. 64). This application was made primarily to determine the effect of bituminous roads on the

FIG. 64. Testing of traffic paints along Brooklyn waterfront.

color of the paints. Since the location was between docks and warehouses, it was attended by a great variety of abuses and, seemingly, offered a splendid opportunity for testing the paints' wearing qualities. However, owing to many loadings and unloadings of freight, the abuse frequently was localized at one or two stripes. Because of this uneven wear, durability ratings from the asphalt site were unreliable and were discarded.

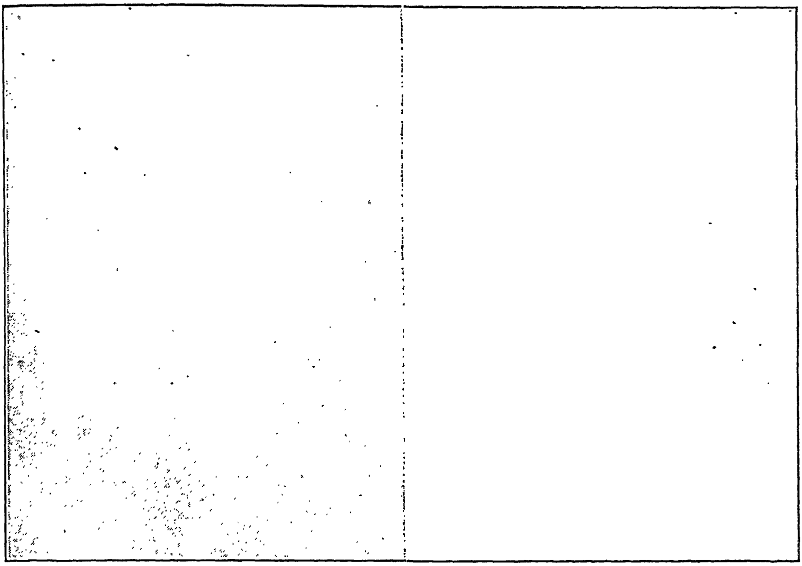
The forthcoming discussion of durability, therefore, will be based solely on the results from the concrete road test, while that of color will be from both applications.

Periodically, complaints have been leveled at the California formula, not because of any performance shortcomings, but because of difficulties encountered in its manufacture. In the first place, tung oil is not soluble in the three solvents used (acetone, butanol, and ethyl alcohol). When added to this combination, the tung oil will separate

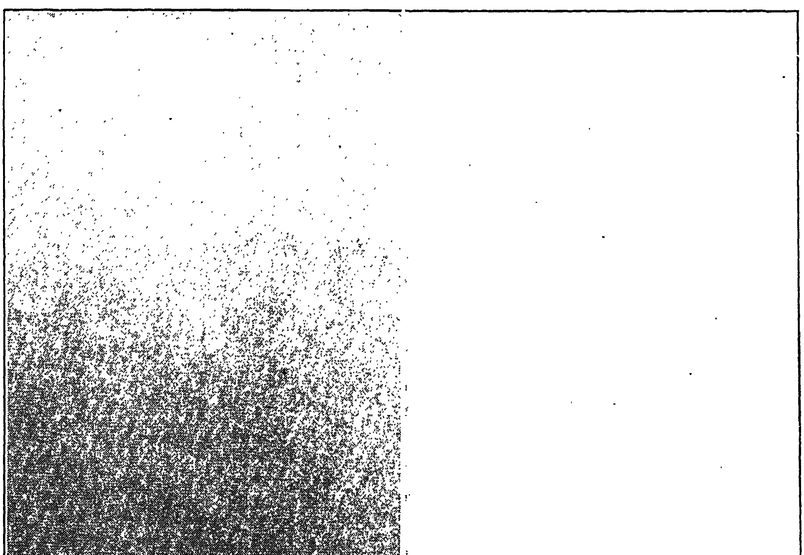


These eight panels represent paints formulated with different oils. Note that tung oil was the only oil to suffer precipitation.

FIG. 65. Dip-coated metal panels of traffic paints. (Actual size.)



E-4 Oiticica oil E-5 Fish Oil



E-6 Dehydrated castor oil E-7 Castor oil

Formula for all eight paints: 55% resin vehicle consisting of 35% manila DBB and 65% solvent, whose composition in parts by volume is 15 oil, 17 butanol, 34 acetone, and 34 denatured alcohol; 45% pigment which in turn consists of 63% titanium-barium material and 37% asbestine.

FIG. 65. (*Continued.*)

immediately unless resin be present to act as a flux for the oil and the three solvents, as is true in the finished vehicle. The vehicle, once prepared and apparently stable, may or may not suffer precipitation of the tung oil at a later date.

The authors have had on hand several different batches of the California vehicle which, after two months' stability, suffered precipitation of the oil during the third month. Other samples of the same formula have been kept for eight months with no loss of stability. A possible explanation may lie in the order in which the components are blended to form the solvent. The temperature to which the finished vehicle is subjected may also be a factor.

The tung oil vehicle also shows erratic stability in the completed traffic paint. Most of the paints prepared with tung oil when re-examined after standing on the shelf for several months contained particles of precipitated oil. No paint prepared with other oils contained such particles. Likewise, in Series B where the tung oil was combined with coal-tar solvents (in which it is completely soluble), no precipitation occurred.

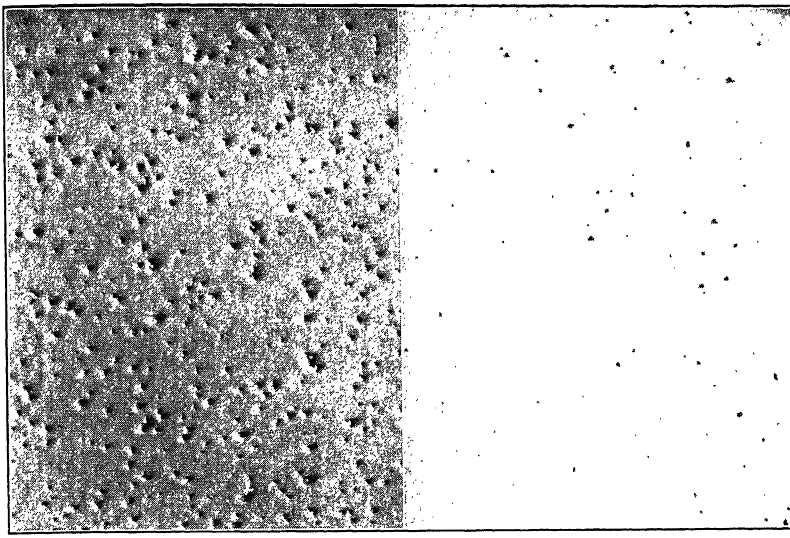
In order to study stability, metal panels of all the paints were prepared. The panels were dip-coated and allowed to dry in a nearly vertical position. Many of the films were marred by the presence of particles of precipitated tung oil. Photographs of a number of these panels are included.

In Series A (containing tung oil, acetone, and ethyl and butyl alcohols—the standard California vehicle), three out of four panels were coated with particles of precipitated tung oil. One of these (A-2) is shown in Fig. 65.

The panels of Series B (containing tung oil and coal-tar solvents) were smooth without instability. The panel of B-2 is the only one of Series B to be included in Fig. 66. Its smoothness was typical of all the paints in this series.

The two paints of Series C (containing tung oil but with alcohol replacing the acetone of the A series) yielded panels whose films were characterized by large distribution of precipitated tung oil particles. Figure 66 includes a photograph of the C-2 panel. This illustration represents a severe instance of tung oil precipitation in an alcohol-base traffic paint.

The vehicles of the paints in Series E were duplicates of those used in the A series save that other oils were substituted for the tung oil specified therein. The oils were linseed, soybean, perilla, oiticica,

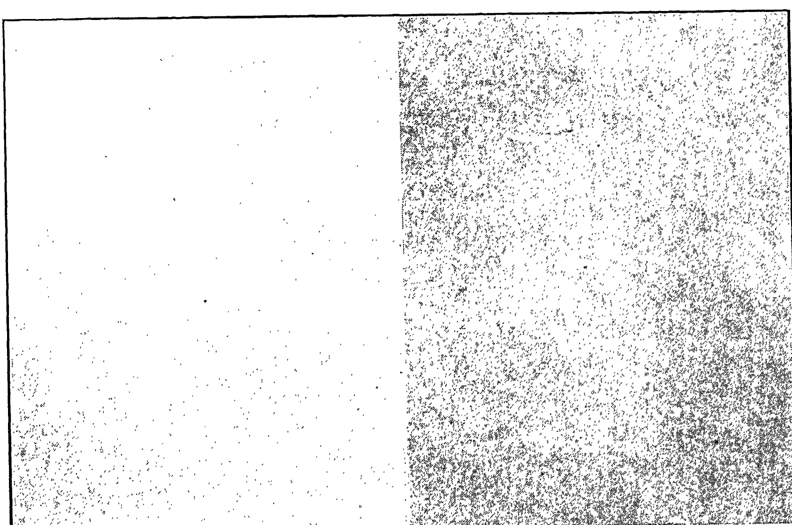


C-2

An exceptionally bad case of tung oil precipitation in an alcohol-base traffic paint.

S-1

The standard California traffic paint. No asbestine present. Vehicle composed of DBB, tung oil, and ethyl and butyl alcohols.



B-2

No alcohol or acetone present. Vehicle composed of black east india, tung oil, and coal-tar solvents. Note the perfectly smooth film obtained when tung oil is used in conjunction with coal-tar solvents.

F-1

One of the few stable tung oil-alcohol paints prepared. Vehicle composed of DBB, tung oil, acetone, and ethyl and butyl alcohols plus a very small amount of elemi.

FIG. 66. Dip-coated metal panels of traffic paints. (Actual size.)

fish, dehydrated castor, and castor. Panels prepared from these paints were smooth. The vehicles, portions of which had been kept for observation, also maintained their stability. Photographs of the panels from Series E are given in Fig. 65. To make this collection complete, the panel of the tung oil paint (A-2) was also included.

With the exception of small additions of elemi, the three paints of Series F were duplicates of A-2. Of these, two panels were smooth and the third was slightly marred by roughness. Of the stored samples of vehicles, only one contained particles of precipitated tung oil. A photograph of the F-1 panel (one of the few stable tung oil-alcohol paints prepared) is given in Fig. 66.

Paint J-1, the only paint in the J series that did not contain tung oil, was likewise the only paint of this series whose film was free of roughness. Series J was a study of the effect of the ratio of oil to resin. As such, the first paint contained no oil, whereas the succeeding ones were made with increasing amounts of oil. Panels of the first four paints are given in Fig. 67. The progressive increase in roughness as the tung oil content increases is readily apparent in this set of photographs.

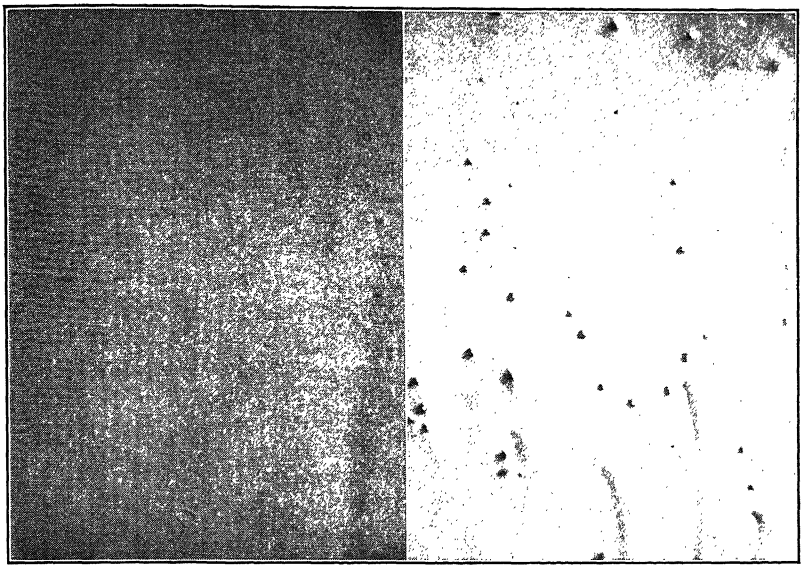
All the panels of Series H (tung oil-alcohol base) showed roughness although in two of them only to a slight degree.

In anticipation of possible comment that the roughness of the previously described paint films was due to their content of asbestine, the panel of S-1 (which contained a tung oil-alcohol vehicle but no asbestine) is included in the photographs of Fig. 66 to show that this effect appears even in the absence of asbestine.

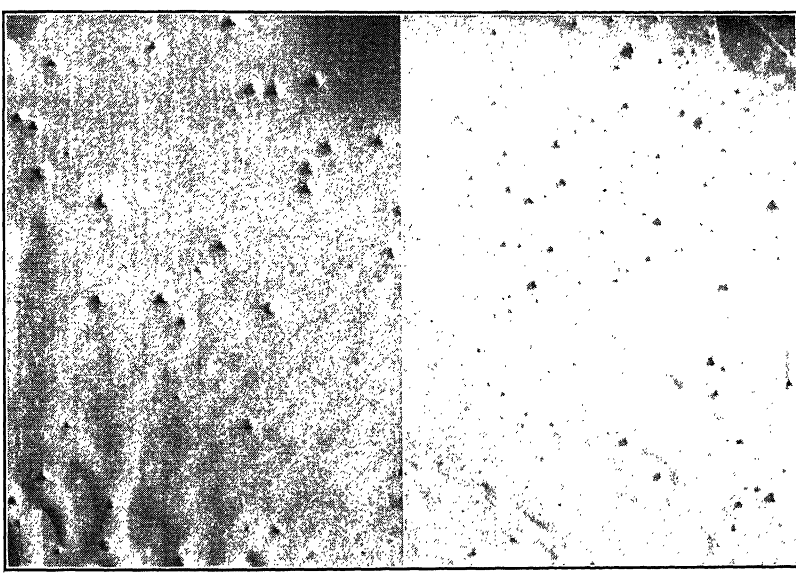
Some of the paints were made with tung oil taken from laboratory stocks while others were made with newly purchased oil taken from a previously unopened can. Each source of oil yielded both stable and unstable products.

A summary of the thirty-four paints prepared reveals that of twenty-two made with tung oil, acetone, ethyl alcohol, and butanol, only three were stable, whereas every one of the twelve paints made without tung oil, or with tung oil and coal-tar solvents, was completely stable.

The possibility exists, but has not been investigated, of securing stability in tung oil-alcohol traffic paints by the substitution of small amounts of coal-tar or petroleum solvents for part of the alcohol. Such additions would cause no precipitation of resin, as alcohol solutions of manilas can be safely reduced to this extent with these solvents.



J-1 0% Tung oil J-2 2.7% Tung oil



J-3 5.5% Tung oil J-4 8.3% Tung oil

The above four panels readily show the growth in roughness with an increase in tung oil content.

FIG. 67. Dip-coated panels of paints made with varying amounts of tung oil. (Actual size.)

In order to avoid precipitation of tung oil in the preparation of traffic paints, T. E. Stanton[4] advocates the following procedure:

1. Add the butyl alcohol to the acetone, mix well, then add the denatured alcohol and agitate for ½ hour.
2. Add raw China wood oil and mix for one hour.
3. Add the resin, mix from 8 to 10 hours and let stand approximately 12 to 14 hours and then strain; the liquid is the finished vehicle.
4. In grinding, start with about 25 per cent of the vehicle and grind with the Titanox and prussian blue from 3½ to 4 hours.
5. While grinding, the rest of the vehicle should be gradually introduced into the mixing vat and continually agitated while adding the ground pigment and then mixed for 2½ to 3 hours after completion of the grinding.
6. After completing the grinding, 5 gallons of amyl acetate are added to each 500-gallon batch of the finished product.

Stanton reports this method to be foolproof if followed explicitly. However, it is possible that as the mixture of resin, oil, and solvents is allowed to settle for 12 to 14 hours before filtering, any insoluble portion of the tung oil would be filtered out along with the insoluble matter from the resin and perhaps not be noticed.

From the experiments conducted by the authors it appears that the use of dehydrated castor oil or castor oil in place of the tung oil gives stable solutions.

The following discussion of durability is based upon a six-month road test on a concrete highway. Photographs of most of the test stripes are included. All photographs were taken six months after application.

Series S. The only paint in Series S was one prepared according to the California traffic paint specification and used as a standard in this investigation. This paint showed poor initial wear and during the first few months of test was the worst worn of all the paints under test. At the first inspection (four weeks) the stripe showed chipping. There are indications that the addition of asbestine yields a more satisfactory traffic paint film than does one formulated with straight titanium-base pigments.

The photograph of the test stripe is given in Fig. 68.

Series A. In this series the importance of the hardness of the resin was under study. A soft resin will confer elasticity upon the paint film but might lack the abrasion resistance of a harder resin.

On the concrete road, paint A-4, containing a soft manila (MA), was in better condition at the end of six months than paint A-2 which

[4] *Paint, Oil Chem. Rev.,* **102,** No. 15, 15 (1940).

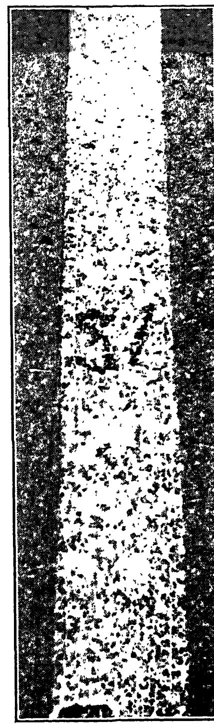
contained a hard manila (DBB). Paint A-3 using a manila of intermediate hardness (loba) gave a film whose durability was intermediate to that of A-2 and A-4.

The paint made with cold-cut congo dust (A-6) was on a performance par with A-4. The whiteness of this paint was equal to that of the manila paints. Photographs of these test stripes are given in Fig. 69.

Series B. This series was similar to Series A in that the resin again was the variable under study.

In the matter of durability there was little choice among the three hard damar type resins used—batu (B-1), black east india (B-2), and pale east india (B-3). The initial wear of B-2 seemed to be slightly better than the other two, but no one was outstanding at the end of six months. The three hard damar paint films suffered more wear than the soft manila film of paint A-4 and were similar to A-2.

The paint containing run congo (B-4) was the only one, of all the paints prepared, whose whiteness could not be termed excellent. Its color was slightly "off" because of the darkness of its thermally processed resin. This resin, nevertheless, gave a paint film of satisfactory whiteness. Despite their content of coal-tar solvents, no bleeding was encountered when the paints of this series were applied to an asphalt road in a supplementary road test.



S-1

(After six months on a concrete road.)

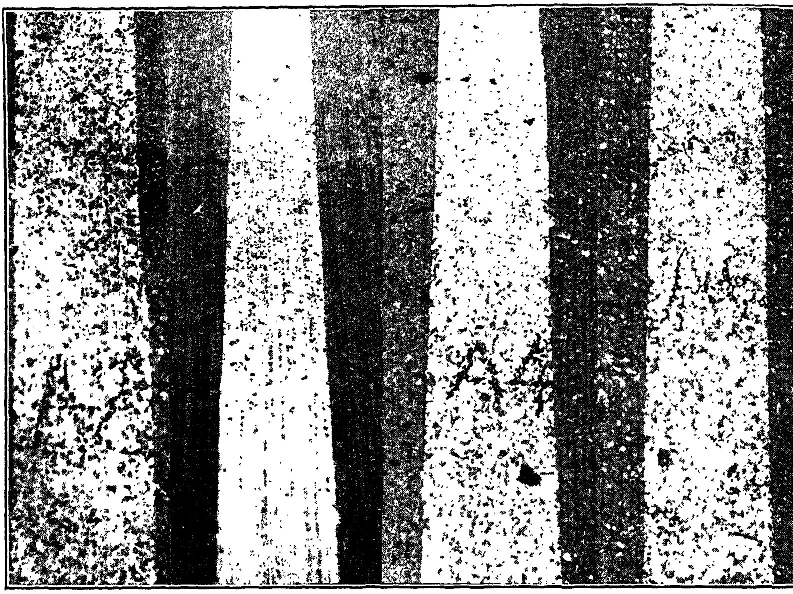
FIG. 68. The California traffic paint. Used as a comparison paint in this study.

The paints from the East India resins gave slightly flatter films than those made with Manila resins. Photographs of the test stripes of Series B are given in Fig. 70.

Series C. In an attempt to determine whether too much film strength was being sacrificed by the use of such volatile solvents as are called for in the California formula, two paints (C-1 and C-2) were prepared. They were similar to A-2 but with its acetone replaced by less volatile solvents. In C-1 the acetone was replaced by ethyl alcohol, and in C-2 the acetone was replaced by equal parts of ethyl alcohol and butanol. As can be seen from the photographs (Fig. 71), the wearing quality of C-2 was slightly better than that of C-1, whereas C-1 showed less wear than A-2. The results indi-

cate that more durable paints can be obtained by the substitution of less volatile solvents for acetone.

Series E. This series deals with the substitution of other oils for tung oil. The tung oil acts mainly as a plasticizer, and is only 6.1 per cent by weight of the finished paint. With such small quantities, the



A-2	A-3	A-4	A-6
DBB	Loba	MA	Congo Dust

(After six months on a concrete road.)

FIG. 69. Variable—resin.

Basic Formula

55% Resin vehicle	45% Pigment
35% (—) resin	63% Titanium-barium pigment
65% "Solvent"	37% Asbestine

durability of the paint is not necessarily dependent upon those properties which normally are demanded in an oil for another use. The results of six months' application to both concrete and asphalt roads show that the colors of all paints made with oils other than tung oil were uniformly excellent.

The different oils were: linseed (E-1), soybean (E-2), perilla (E-3), oiticica (E-4), fish (E-5), dehydrated castor (E-6), and castor (E-7). Except for the oil substitution, the paints of Series E were duplicates of the A-2 formulation.

It can be seen from the photographs (Fig. 72) that a number of other oils can be satisfactorily substituted for tung oil. Only one of

the oils tested gave a paint film with poorer durability than did tung oil. Castor oil (E-7) in particular gave a very good film. This film remained unmarked for five months, and began to show wear only during the sixth month. The dehydrated castor oil paint (E-6) was rated second best. At the first four-week inspection, it was given a

B-1	B-2	B-3	B-4
Batu	Black East India	Pale East India	Run Congo

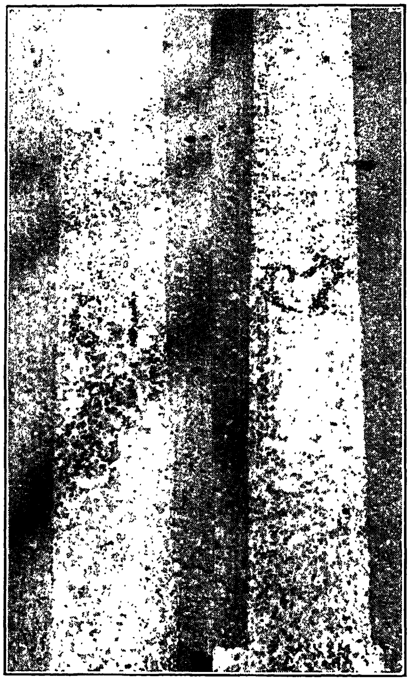
(After six months on a concrete road.)

FIG. 70. Variable—resin. The basic formula is the same as that for Series A save that coal-tar solvents were used.

rating of "slightly worn" and was not among the best of the various oils used. However, during the next five months the stripe suffered negligible further wear and at the end of six months its performance rating was second only to the castor oil paint film.

Paint E-5, containing fish oil, showed good initial wear, being unmarked for several months. During the third month slight signs of wear appeared and continued to grow moderately. The test stripe was in fairly good condition at the end of six months.

Paints containing linseed (E-1), soybean (E-2), and perilla (E-3) oils showed progressive wear from the beginning of the road test. There was no initial period of freedom from wear. As shown in Fig. 72, paints formulated with these three oils yielded films that were still in a serviceable condition after six months.



C-1 C-2

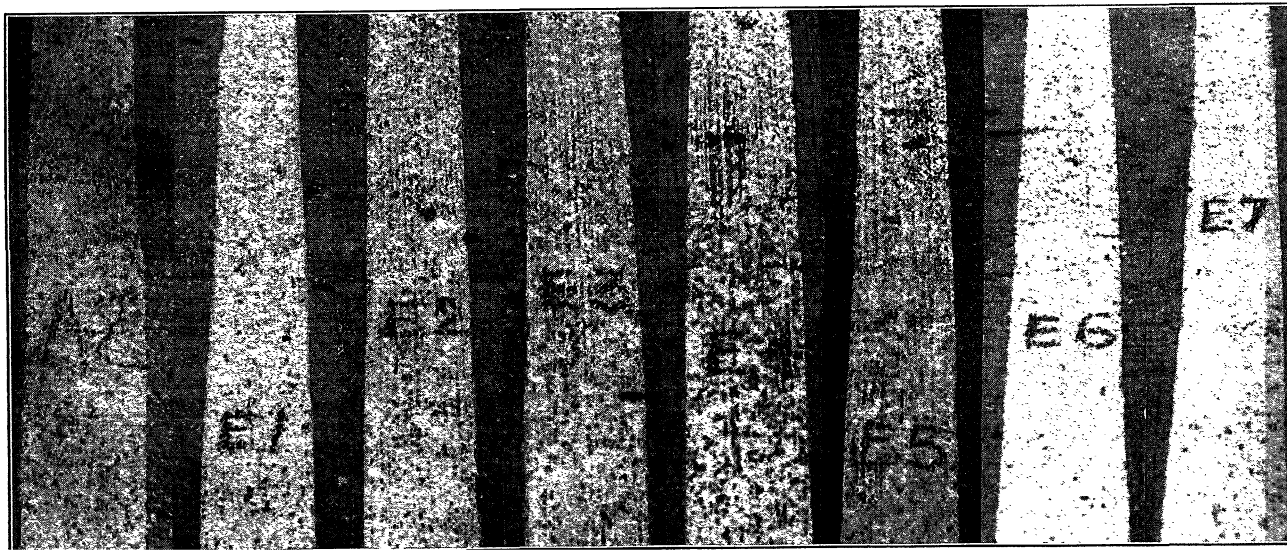
(After six months on a concrete road.)

FIG. 71. Variable—volatility of solvent. The solvent of C-2 is less volatile than that of C-1.

Of all the oils used in place of tung oil, oiticica (paint E-4) was the only one which failed to give a traffic paint film of satisfactory durability.

Series F. Three paints were prepared containing varying amounts of elemi (a soft, plastic resin) in an attempt to determine whether road adhesion could be improved. Such additions proved to have no effect on adhesion or durability, but they did have an effect on the flow of the paint.

In the application of the paints to the road, it was necessary to apply a definite volume as a uniform film to each stripe. This meant



A-2	E-1	E-2	E-3	E-4	E-5	E-6	E-7
Tung	Linseed	Soybean	Perilla	Oiticica	Fish	Dehydrated castor	Castor

(After six months on a concrete road.)

FIG. 72. Variable—oil.

Basic Formula

55% Resin vehicle
- 35% Manila DBB
- 65% "Solvent" (as follows in parts by volume)
  - 15 (   ) oil
  - 17 Butanol
  - 34 Acetone
  - 34 Denatured alcohol

45% Pigment
- 63% Titanium-barium pigment
- 37% Asbestine

measuring out the paint in a rapid passage of the applicator to ensure equal linear disposition, followed by another passage of the applicator over the wet stripe to "iron out" the stripe to its full 6-in. width. The high volatility of the solvents and the resulting quick setting of the paint often made the second travel of the applicator difficult because of tackiness. In elemi-containing paints, the flow was so improved by the addition that it was not necessary to go over the stripe a second time. Moreover, a test second travel showed that the tackiness of the wet film had been greatly reduced.

Elemi can be added in amounts up to 5 per cent (greater amounts were not tried) on the weight of the finished paint without causing any tackiness in the dried film.

All three elemi-containing paints were in the same state of wear, and were similar to the manila paints of Series A.

Series H. The eight paints of Series H were prepared in an attempt to determine the importance of the pigment-to-binder volume ratio. Using two different pigment compositions, two sets were made with pigment volumes of 28, 34, 40, and 46 per cent. For the first four paints, 63 per cent titanium-barium (30 per cent TiO_2) and 37 per cent asbestine were used; for the second four, titanium-calcium pigment was substituted for the titanium-barium pigment.

For three months there was but slight wear in all eight paints. Beginning with the fourth month, however, signs of wear appeared, and at six months all were in varying stages of wear. The 28 per cent pigment volume paints were inferior to the paints of higher pigment volume. There were no differences between the 40 and 46 per cent pigment volume paints, although the superiority of one might be shown with a longer period of test. The 34 per cent pigment volume paints were of intermediate durability.

There was no choice to be made of the relative durability of paints prepared with titanium-barium or titanium-calcium pigments. Subsequent tests revealed titanium-calcium pigment to be below titanium-barium pigment in durability.

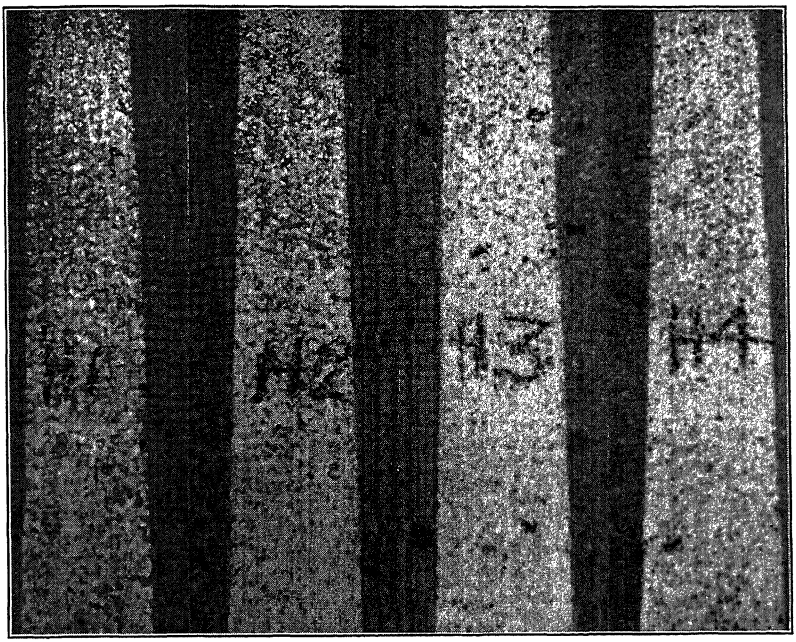
On a black asphalt road the hiding power of the lower pigment volume paints was poor. Indications were that for good hiding power on bituminous roads, the pigment volume (for the pigment compositions studied) should be at least between 34 and 40 per cent and preferably closer to the latter. The pigment volume of the California formulation, containing straight titanium-barium pigment, is approximately 34 per cent.

Photographs of H-1, H-2, H-3, and H-4 are given in Fig. 73.

Series J. The paints of Series J were made with varying oil-to-resin

ratios. As a starting point, the first paint of this series (J-1) was prepared with a zero oil content. The ratio of oil to resin was increased for each succeeding paint.

Within four weeks of its application, J-1 had suffered a wide distribution of pock marks. The marks did not penetrate through the film to the road surface until the second month. J-2 was similarly affected, but to a lesser extent. For the first four months, the last



H-1	H-2	H-3	H-4
28% P.V.	34% P.V.	40% P.V.	46% P.V.

(After six months on a concrete road.)

FIG. 73. Variable—pigment volume. The same constituents were used in all four paints but were combined in the proper proportions to yield the above pigment volumes.

three paints of this series (J-3, J-4, and J-5) showed negligible wear and there was little choice among them. Their films were free from pock marks. During the fifth month, however, J-3 began to show signs of wear. By the end of six months all five paints were in various stages of wear with the condition of the first two by far the poorest.

Both J-1 and J-2 suffered excessive wear at the points of tire contact, whereas the wear of J-3, J-4, and J-5 was evenly distributed.

J-1 1 Resin 0 Oil | J-2 9 Resin 1 Oil | J-3 8 Resin 2 Oil | J-4 7 Resin 3 Oil | J-5 6 Resin 4 Oil

(After six months on a concrete road.)

FIG. 74. Variable—resin-to-oil ratio. The same constituents were used in all five paints but were combined in various proportions to yield the above resin-to-oil ratios.

Inspection of the test stripes revealed that in the case of J-1, J-2, and J-3, the lack of sufficient plasticizer had resulted in the formation of a network of very fine cracks throughout the surface of the film. J-4 and J-5, with their higher contents of oil, were free from this type of failure.

The dependence of traffic paint films on their oil content for durability is readily seen from the photographs in Fig. 74.

On bituminous roads, high oil content causes dirtying of the stripe. For spirit traffic paints containing oil without drier, supplementary tests on an asphalt road indicate that the maximum ratio of oil to resin should be about 1 to 4. The maximum oil content for this type of formulation, therefore, becomes approximately 6 per cent on the weight of the finished paint. This percentage, incidentally, corresponds closely to the oil content of the California formula (6.1 per cent). Higher oil contents than this give films of greater durability on concrete roads, but on bituminous roads will cause premature dirtying of the stripe.

On a concrete road, the maximum oil-to-resin ratio appears to be below 4 to 6. On a total weight basis, the oil content of this paint was 11 per cent. For traffic paints of this type, the maximum ratio of oil to resin is probably close to 3.5 to 6.5, or about 9.7 per cent oil on the weight of the finished paint.

A number of formulations such as No. 523 appear to merit recommendation as being superior to the California specification. The main changes are an increase in pigment volume, inclusion of some asbestine, and the use of raw and dehydrated castor oils.

Formula 523—Improved Traffic Paint

53 per cent resin vehicle

33 per cent manila DBB
11 " " oil*
56 " " solvent made as follows, in parts by volume:

100 per cent

20 butanol
40 acetone
40 denatured alcohol

* Tung oil should give satisfaction if it can be maintained in complete solution. Dehydrated castor oil is to be preferred, however, because of its stable solution in the solvents used. Castor oil may also be used, although it is possible that under certain conditions on heavily traveled roads a castor oil paint might not give quite so good a performance as would the tung or dehydrated castor oil paints. On the other hand, on lightly traveled roads where ultimate failure occurs through weathering rather than through traffic wear, the more flexible film obtained with castor oil might be preferred.

47 per cent pigment	63 per cent titanium-barium pigment (30 per cent TiO_2)	
	37 " " asbestine FT	
	100 per cent	
100 per cent		

Method. Using enough manila DBB to yield a vehicle containing 33 per cent of actual resin after filtration, the solution of resin in the solvents is prepared and filtered. The oil is then added to complete the vehicle. The paint is ground in a ball mill as a 60 per cent pigment paste using all the pigment. After 3 to 4 hours of grinding, the remainder of the vehicle is added and grinding continued for 1 to 2 hours. If necessary, 1 per cent by volume of amyl acetate may be added to improve the flow along with any blue pigment paste used to enhance whiteness.

In the field of oil-base traffic paints, the various state specifications frequently do not specify the varnish resin, but merely require the use of a certain amount of a varnish of definite oil length or solids content. On the other hand, they may require a varnish of a quite definite composition with the resin, oils, length, and solids content rigidly specified.

For this type of traffic paint the east india resins are widely used. East india resin traffic paints possess good abrasion resistance, light color, and a desirable flatness. Batu is usually chosen because of its low cost. Examples of natural resin oil-base traffic paints may be found among the specifications in Table CXVIII.

Ceiling Paints. Although an ordinary kalsomine ceiling paint possesses the advantages of low cost and good whiteness, it shows poor adhesion and poor film strength. These properties may be secured by the use of oil-base paints or paints of the traffic type. Traffic paints are particularly suitable for this application because of their good adhesion and color retention. In the oil-base type, damar should be used to secure freedom from after-yellowing. For ceilings the softness of damar films is not objectionable, although this property can be improved by the addition of harder resins or ethyl cellulose.

Wall Paints. Natural resin paints of the traffic type also find application as wall paints for the mass refinishing of apartment and mill walls. Here, an inexpensive, quick-drying, sprayable, serviceable paint is required. Mill paints may also be formulated using oil varnishes prepared from various grades of natural resins as the vehicle.

The following formula represents a mill-white vehicle that is non-reactive, very light in color, and that possesses excellent color retention and dries satisfactorily overnight.

Formula 524—Mill-White Vehicle

50 Gallons in Oil Length

100 lb. Batavia damar A/E
13 gal. China wood oil
37 gal. heavy-bodied soybean oil
79 gal. mineral spirits

Plus driers equivalent to 0.5% lead, 0.03% cobalt and 0.01% manganese as metals based on the weight of oil present in the varnish.

Procedure: Heat the China wood oil alone to 300°F. Sift in the damar. Heat to 520°F. and hold for body at that temperature. Add the soybean oil. Further heating may be necessary for a short time for complete clarity. Allow to cool to 400°F. and add the mineral spirits. Then add the driers.

Similar non-reactive vehicles may be prepared using the east india resins—pale, black, and batu.

Because of the tendency of alkyd resin enamels to suffer discoloration upon baking, it has been common practice to fortify these resins for hardness and color stability by the addition of maleic-anhydride resins. Experiments show that Batavia damar may be similarly employed as a modifying agent. Using purchased commercial samples of typical alkyd resins, it was found that the addition of 5 to 10 per cent of Batavia damar on the weight of alkyd definitely improved the color of baked films. In every case, enamels containing Batavia damar as the modifying agent showed less discoloration upon baking than did the same enamels lacking modifying resins. The damar had no adverse effect upon film hardness. Except in the case of those alkyds possessing high gloss in their own right, the gloss of the prepared enamels was increased considerably by the addition of damar.

As modifying agents for baked alkyd finishes, the experiments showed that there was nothing to choose between damar and the maleic-anhydride resin used. The effects of each were for all practical purposes the same.

The damar is dissolved in a petroleum or coal-tar solvent and blended with the alkyd solution. The damar need not be dewaxed. Such enamels are simple in both their formulation and preparation. A typical one follows.

Formula 525—Damar-Modified Alkyd Enamel

50 per cent vehicle	
	90 per cent of a 50 per cent alkyd resin solution
	10 per cent of a 50 per cent Batavia damar solution
50 per cent pigment	
	75 per cent titanium dioxide
	15 per cent antimony oxide
	10 per cent zinc oxide
100 per cent	

Metal Primers. The East India resins are used in metal primers because of their cheapness, good adhesion, and their tendency towards flatness of film. This latter property can be fully developed by the avoidance of excessively high temperatures during both the running of the resin and the cooking of the varnish. (See discussion of flat varnishes in varnish chapter.)

The unpurified wax residue from the dewaxing of damar sometimes finds its way into the preparation of cheap paints such as barn paints or similar compositions in which color or absolute purity are not important.

Formulations for a quick-drying (air-drying) vehicle, occasionally required for drum or barrel paints, are illustrated in Table CXX.

TABLE CXX

Formula No.	526	527	528	529
Pale east india bold	100 lb.	100 lb.	. . .	. . .
Batavia damar A/E	. . .	. . .	100 lb.	100 lb.
Bodied linseed oil	16 lb. (2.05 gal.)	. . .	16 lb. (2.05 gal.)	. . .
China wood oil	. . .	16 lb. (2.05 gal.)	. . .	16 lb. (2.05 gal.)
Petroleum thinner (Boiling range 200–275°F.)	. . .	. . .	116 lb. (18 gal.)	116 lb. (18 gal.)
Toluol	116 lb. (16 gal.)	116 lb. (16 gal.)	. . .	. . .
Oil length (gal.)	2.05	2.05	2.05	2.05

Procedure: Grind the resin to small pieces. Mix all ingredients, including driers, by cold cutting. Driers added are equivalent to 0.5% lead and 0.02% cobalt as metals on the weight of oil present.

Properties: All the vehicles will dry within 1 hour. Numbers 528 and 529 are lighter in color and clearer.

Luminous Paints. The first essential of a medium for luminous paints is that no constituent of the vehicle, including the solvent, shall react with the luminescent pigment (phosphor). Constituents must be as neutral as possible. Highly acidic resins or solvent esters which hydrolyze to form acids should be rigorously avoided. Low acid value resins are satisfactory, because their acidity is neutralized by a small amount of phosphor.

As most oils are quite unsuitable for the preparation of luminous paints, the formulator is limited to resinous or cellulosic media, although the latter, unless specially treated, also act to weaken the glow.

Damar has been recommended as a medium because of its low acidity, good color, and ready solubility in petroleum and coal-tar solvents (the preferred solvents in luminous paint formulation). The initial tackiness of damar films can be overcome by zinc resinate. The following vehicle has been suggested by Bryson:[5]

Dewaxed damar	40 per cent by weight
Neutral zinc resinate	10 " " " "
Toluol	50 " " " "

A copal ester with a low acid value can be dissolved in petroleum or coal-tar solvents to yield a vehicle for luminous paints. It is necessary to add a small amount of plasticizer. The initial yellowish color is moderated by the bleaching action of sunlight.

Van Heuckeroth[6] found that vehicles for luminous paint could be made from damar in turpentine. Reduction of particle size of the pigment reduces luminous properties. Wakenhut[7] confirmed the suitability of damar for this purpose.

Gloss Improvement of Outside Paints. Resins find application in outside paints in the form of spar varnishes added to the paint to improve its gloss. For such use, a varnish of 35-gallon length is quite satisfactory.

[5] H. C. Bryson, *Paint Industry Magazine,* **55,** 119 (1940).

[6] A. W. Van Heuckeroth, *Am. Paint Varnish Mfrs. Assoc., Circ. No. 440,* pp. 237-8 (1933).

[7] A. Wakenhut, *Farben-Chem.,* **2,** 454-7 (1931).

CHAPTER XXII

PRINTING INKS

Resins have long been the stand-by for a variety of the so-called "specialty inks," both oxidizing and non-oxidizing in nature. Examples are gloss, "non-rub," "non-scratch," carton, food and candy wrapper, cellophane, glassine, aniline, wax-set, water-set, soap wrapper, metallic, bottle-printing, and gravure inks.

The specialty inks are applied to surfaces other than paper or must possess properties not found in a drying oil film alone. Resins are utilized in the majority of applications. The damars and the east indias are pale in color, whereas batu and black east india are dark. They all have the common property of being oil soluble by simple cooking. The fossilized naturals have to be run to make them oil soluble, and the resulting color of the varnish may be too dark for light-colored inks. The damars and the east indias produce light-colored, non-reactive varnishes whose films may be hardened and toughened by the addition of other resins such as phenol-aldehyde or maleic-rosin resins.

The difficulties in specialty inks are mainly concerned with tack. Unless a good grade of paper can be used, troubles range from "picking" to "pulling from the grippers" and actual tearing of the sheet or web. "Slip sheeting" is necessary to prevent sticking of the piled sheets, or, if a web-fed press is used, a "traveling tympan" is employed. Where formulation difficulties prevent the use of gloss inks or when low-grade paper must be used, overprinting is usual to fulfil the gloss requirements. Frequently, as in label varnishes, the overprinting serves the twofold purpose of enhancing the gloss and providing a protective coating for the printed surface. Overprinting is done from a solid plate which covers the entire printed surface. The varnish consists of resin, drying oil, small amounts of thinners and waxes, and appropriate driers. The drying time should be low and the dried print should not possess tack. The overprint varnishes are quite sticky and slip sheeting is the rule rather than the exception. Some practice has employed spray guns containing gum arabic or similar solutions to prevent sticking.

Work on overprint varnishes has shown that the tendency of damar

to cause after-tack can be overcome. An important development for specialty inks is the use of purified damar wax. Damar wax is oil soluble without being run and produces hard, tough films which are resistant to abrasion and free from after-tack.

Label varnishes, are, in effect, overprint varnishes, but the trade chooses to refer to them as spirit varnishes. In formulating an ink to be spirit varnished, the pigments must be selected from those which do not bleed in the solvent of the varnish.

Label printing is usually a relatively cheap process. Overprint varnishes are occasionally used but the predominating practice is spirit varnishing. The varnish is applied in a continuous film covering the entire web and is dried with the aid of heat. The use of a spirit varnish obviates many of the difficulties inherent in the use of drying oil-resin varnishes upon inferior grades of paper. These include picking of the stock and lower rates of production owing to the longer drying time required. The film is less flexible and less durable than that of an oleoresinous varnish. It serves the purpose well, however, in that it produces a finish having high gloss and adequate protective life as well as a high production rate with consequent lower cost.

Manila is most extensively used for this purpose, for it combines satisfactory color with harder and more durable films. Damar softens at too low a temperature. The varnish is usually a cold cut manila in alcohol with or without the addition of a plasticizer. Similar Manila copal spirit varnishes are used in the production of aniline inks.

The printing industry has followed the trend toward increased rates of production which may be in turn translated into terms of higher and higher press speeds. A point was reached at which the limiting factor was no longer the presses, which are capable of still higher speeds, but the drying time of the inks in use. Inks had to be developed which would dry almost instantaneously when applied to paper and still remain wet on the plates for an appreciable period in the event of a temporary shut-down. This has been accomplished by two methods, first, by contact with some setting media as in the case of wax-set or water-set inks, and second, the prevalent method, by application of heat. In both, resins constitute the binding agent.

If an ink which consists essentially of a pigment dispersion in a resin solution containing appropriate solvents be printed upon a high-speed cylinder press and the web then passed through a heated zone, drying may take place in two different ways. Assuming the temperature of the heating zone to be such that the solvent vapors are not raised to their kindling temperature, drying will be a function of sol-

vent removal by the concomitant effects of an increased rate of vaporization and greatly increased rate of absorption into the paper caused by the decrease in the viscosity of the vehicle. In the second case the temperature is adjusted to above the kindling temperature of the solvent and the solvent vapors are burned. In both, the temperature exceeds the kindling temperature of the paper. The speed of the web, however, does not allow sufficient time in the heating zone for scorching to occur.

A great variety of surfaces have been printed in this manner: paper, cellophane, glassine, and sheet metal for example. Although these methods are not likely to displace the oxidizing type of inks in the small print shop because of the high cost of the necessary heating and exhaust installations, they are making progress in the fields of volume production. Damar, batu, and pale east india are suited to these applications. Particular attention is merited by the characteristics of damar wax and by the possible application of batu wax in a similar manner.

Natural resins in printing inks are restricted to the preparation of overprint varnishes, label varnishes, and specialty inks. Analysis of the problems involved in the formulation of a printing ink will show the reason for this condition. Newspaper inks are consumed in very large tonnages. They are simple, consisting of pigments such as carbon black dispersed in a vehicle such as a petroleum fraction. From the viewpoint of cost, resins cannot ordinarily be used even if their application might confer some advantage to the ink.

Tonnage inks for printing magazines consist of pigments and extenders dispersed in vehicles containing drying oils or varnishes with or without waxes, greases, driers, or other ingredients added to secure specific properties or to suit the ink to definite conditions. Pigment and extender contents vary from extremes of about 10 to 75 per cent on the basis of the finished ink. Inks varying from 10 to about 25 per cent in pigment content are used for newspaper printing and on high-speed magazine presses. Newspaper inks dry by absorption of the vehicle by the paper stock. Magazine inks used on high-speed presses may dry by oxidization or may be dried by a combination of vaporization and absorption aided by the application of heat.

In the formulation of any printing ink, the factors of greatest importance are: drying time, body or consistency, flow, penetration, and tack or stickiness. Each must be easily adjusted to the variations of press, speed of printing, paper, etc., coincident with the specific job. Pigment content is seldom an appreciable variable, as the tendency is

toward inks of high color strength thus permitting the use of thin ink films. Drying oils must usually be employed as the largest volume of printing utilizes well-sized and well-calendered paper or other relatively non-porous surfaces upon which the effect of penetration is negligible. Thus, in order to maintain an adequate drying schedule, the vehicle must consist largely of drying oil. Since the quantity of the vehicle cannot be varied to any great extent, the necessary range of body, flow, penetration and tack must, therefore, be obtained through the use of a series of lithographic varnishes (drying oils heat-bodied to different viscosities).

At first glance it would appear that there still exists ample opportunity for the inclusion of a resinous constituent. However, there are still further requirements to be considered. Extenders cannot be eliminated as they control to a large extent the degree of opacity and gloss or flatness of the print as well as the specific gravity of the finished ink. The substitution of resinous varnishes for lithographic varnishes presents a number of difficulties. Inclusion of resins renders the control of tack, flow, and drying time difficult.

In the printing of a series of process inks, the "first-down" color must have the heaviest body and greatest amount of tack. The remaining inks must have a decreasing degree of tack in the order in which they are to be printed. Failure to maintain a proper tack relationship between inks for process printing will result in a transfer of the inks already printed from the paper back to the plate, ruining the printing job and contaminating the ink in the fountain. Care must be taken that the first-down color does not have sufficiently high tack to exhibit "picking" at the press speed on the particular stock to be used. Tack must be adjusted to a nicety. The inclusion of resins in any appreciable quantity tends to increase tack to a point beyond that permitting satisfactory printing.

In tin lithography, alkyd resin vehicles for printing inks are analogous to alkyd baking enamels. The inclusion of 5 to 10 per cent of damar will markedly inhibit the tendency to after-yellow as well as enhance the gloss of the dried film. The same advantages are applicable to inks for printing on sheet metal, collapsible tubes, etc.

The use of damar and the copals in gravure ink is well known, as is also the use of batu in high-speed rotogravure. In Europe non-inflammable vehicles for high-speed gravure work have been prepared from combinations of Manila copals and sulfonated oils.

Some special applications of resins in inks are to be noted. All the

natural resins have been proposed for incorporation with chlorinated rubber in printing inks.[1]

Kauri, elemi, accroides, and Manila resins have been proposed for wood-grain effects in inks consisting primarily of a resin dispersion. The resin is dissolved in a mixture of terpineol and higher alcohols and emulsified with water by the use of ammonium hydroxide.[2]

Hiroe or pale east india Macassar finds application where dull inks are required. In this case, the East India resins are used for "flat" finishes.

Most of the natural resin varnishes, each with its specific properties, find application in ink manufacture where the varnish is employed as a vehicle.

Photogravure inks may be made of volatile hydrocarbon solvents which evaporate rapidly, thus hindering penetration of the ink into the paper and drying mainly by evaporation. A typical example consists of 72 parts of chrome yellow and 90 parts of barytes extender in a vehicle consisting of 60 parts of damar in 98 parts of a neutral fraction. Penetration or lack of penetration may be controlled by the boiling range of the damar solvent.

Metallic inks using metal pigments are often made with low acid number natural resins, such as damar and the pale east indias. Because the pigment and resin may react, high acid materials such as the manilas are avoided.

In inks employed in printing on glass and ceramics, damar provides the necessary tack. Glass inks may be made from damar-linseed oil varnishes with other ink constituents, such as colors or pigments, incorporated in the usual manner.

Damar has been shown to be useful for overprint varnishes for labels. It is practically colorless and causes negligible darkening upon drying. Good quality varnishes may be made if factors such as oil length, drier content, and cooking temperature are controlled. Drying times of tung oil, linseed oil, cobalt drier, and resin ranged from 2½ to 24 hours. Paraffin wax and kerosene additions improved the quality of the varnishes.[3]

[1] H. Hadert, *Am. Ink Maker,* **11** [11] 9 (1933); T. V. Binmore (to N. Y. Belting and Packing Co.), U. S. Patent 1,552,907 (Sept. 8, 1925); *Am. Ink Maker,* **17** [3], 25 (1939); T. P. Sanguinetti, British Patent 472,684 (1936).

[2] C. B. Hemming (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,008,018 (July 16, 1935); *Rev. Paint, Colour, Varnish,* **8**, 348 (1935).

[3] C. L. Mantell and A. Skett, *Paint, Oil Chem. Rev.,* **101** [4], 7 (1939); *Am. Ink Maker,* **17** [3], 41 (1939).

Gum elemi is suggested for utilization in photolithographic inks. The inks are said to be applicable for printing with zinc plates and stone.[4]

Natural resins of the copal type, such as manila loba C and run congo are suitable in inks for wrappers of odor-sensitive products. Since loba resins are light in color, they are desirable where the proper color ink is important. Natural resins of the damar type have been found to impart an odor to the wrapped material, especially to butter.[5]

SUPPLEMENTARY REFERENCES

J. L. Curtis and C. L. Mantell, "The Place of Natural Resins in Printing Ink Technology," *Am. Ink Maker,* **18** [6], 20 (1940).

C. L. Mantell and A. Skett, "Damar in Overprint Varnishes," *Paint, Oil Chem. Rev.,* **101** [4], 7 (1939).

J. H. Holzberger, "Natural Resins for Food Container Inks," *Am. Ink Maker,* **16** [4], 25 (1938).

C. L. Mantell, "Natural Resins for Printing Inks," *Am. Ink Maker,* **15** [5], 29 (1937).

[4] K. Kampmann, *Phot. Correspondenz,* **26**, 564; *J. Soc. Chem. Ind.,* **9**, 413 (1890).

[5] J. H. Holzberger, *Am. Ink Maker,* **16** [4], 25 (1938).

CHAPTER XXIII

EMULSIONS AND WATER DISPERSIONS

For some applications it is desirable to have the natural resins, or their combinations with waxes, stearic acid, asphalts, pitches, and the like, in the form of aqueous emulsions or dispersions. Such dispersions find use in paper coating, sizing, or impregnation; floor, furniture, or automobile polishes; the waterproofing and stiffening of textiles; spirit varnishes in which part of the solvent is replaced by water, and similar applications.

Owing to their high melting points, the natural resins are not readily liquefied so that they may be directly dispersed in water. In solvent solutions or in combinations with other materials, such dispersions are possible. The natural resins of high acid number may be converted into the water soluble or dispersed condition by the formation of resin acid soaps.

Aqueous Alkaline Solutions and Dispersions of Manilas. The Manila resins can be made into water solutions or dispersions by the use of strong alkalies or mixtures of alkalies with borax. Satisfactory dispersing agents include sodium hydroxide; ammonia; ammonia and borax; the mono-, di-, and tri-substituted ethanolamines; morpholine; and the triethanolamine soaps of fatty acids. The soft manilas, such as WS, MA, and MB, or the half-hard manilas, such as the lobas, are more readily soluble in alkaline solutions than are the fossilized types.

Manila Resins in Ammonia and Borax. The manilas cannot be held safely in solution with borax alone, but with the proper pretreatment of the resin can be made to dissolve by the addition of ammonia. The raw resin swells up into a doughy mass when treated with ammonia and borax solution.

In using borax and ammonia to disperse Manila resins, the following procedure may be employed: Dissolve 3 parts of borax in 50 parts of water. Add 10 parts of the powdered resin slowly, with stirring. When the resin has all been added, add enough ammonia to dissolve or disperse the resin.

The Manila resins may be made more readily soluble in ammonia or ammonia and borax solutions by finely grinding and heating just below their softening points for 100 hours. Several months of exposure

to air in the ground condition at room temperature has the same effect.

Manila Resins in Sodium Hydroxide and Ammonia Solutions. Ammonia and alkali solutions are satisfactory where films of high water resistance are not required. They are made by adding the powdered resin to a water solution of the base. An indication of the quantity of base required is given by the acid number of the resin. Using the following equations, this quantity may be calculated. The constants, 0.71 and 0.3, are conversion factors from KOH, used in the determination of acid value, to NaOH and NH_3 respectively.

For alkali solutions, using solid NaOH:

$$\text{Weight in grams of solid NaOH required} = \frac{\text{weight of resin (grams)} \times \text{acid no.} \times 0.71}{1{,}000}$$

This weight of sodium hydroxide is dissolved in the desired amount of water and, with stirring, the powdered resin added slowly. Heating greatly facilitates the process.

$$\text{Weight in grams of ammonium hydroxide required} = \frac{\text{weight of resin (grams)} \times \text{acid no.} \times 0.3}{1{,}000 \times \text{the decimal fraction of ammonium hydroxide which is } NH_3}$$

This calculated weight of ammonium hydroxide is dissolved in the amount of water required and the powdered resin added slowly, while stirring. It is important that no heat be used in dissolving Manila resins in ammonia solutions. The equations indicate minimum quantities of the bases needed.

Manila Resins in Triethanolamine and Morpholine Solutions. When finely ground, manilas such as the hard lobas (manila CBB and DBB) may be dispersed in water by emulsifying agents, such as amines like mono-, di-, and triethanolamine, or the oleates and stearates of triethanolamine. If a small amount of a solvent be permitted, such as an alcohol-water solution, the dispersion takes place more readily, or if the resin be dissolved in alcohol first, then the alcohol solution of the resin may be dispersed in water.

Morpholine, a moderately volatile amine cyclic ether, has been used as an emulsifying agent for Manila resins. Ten parts of ground manila DBB were added to 50 parts of water containing 3 parts of morpholine. A satisfactory dispersion was obtained, which, when permitted to stand for impurities and undissolved resin to settle, gave a clear film.

The films obtained from alkaline solutions of manila may be plasti-

cized by high boiling, water-soluble organic solvents such as butyl Carbitol, glycerin, ethylene glycol. Oleic acid may also be used, but with a slightly different procedure. Ninety parts of manila loba C and 10 parts of oleic acid, by weight, are combined by mixing a portion of the ground resin with the oleic acid in the cold, then heating until liquid and adding the remainder of the resin. The temperature is then raised to 150°C., while the mixture is stirred. A highly viscous mass is obtained which cools to a hard, transparent solid. This solid is ground and agitated overnight on a mixing machine with water and ammonia in the proportions by weight of

15 loba-oleic acid mixture
81 water
4 ammonium hydroxide (28 to 29 per cent NH_3)

The solution can be clarified by filtration or centrifuging. It dries to a rather hard film. By increasing the proportion of oleic acid, solutions which remain tacky after drying and are suitable for use in adhesives, are obtained.

Alkaline Aqueous Solutions of Accroides. Accroides is soluble, with reservations, in aqueous alkalies. With ammonium hydroxide, concentrations from 0 to 25 per cent on the weight of the resin do not result in total solubility. Complete solution can be secured by the use of sodium hydroxide or sodium carbonate. With sodium hydroxide, 10 per cent on the weight of the resin is sufficient to insure complete solubility for resin concentrations of the order of 20 to 25 per cent.

Formula 530—Alkaline Accroides Solution

Powdered accroides	100 parts by weight
Water	300 parts by weight
NaOH	10 parts by weight

The solution is prepared by dissolving the sodium hydroxide in the water, adding the accroides, and agitating. It has a Gardner-Holdt viscosity of A, a Gardner color of 18 +.

When resin concentrations of 40 to 50 per cent are employed with 10 per cent of sodium hydroxide, very pasty or viscous solutions are formed in which, solution of the resin may be incomplete. Solutions containing this higher resin content, but possessing viscosities equivalent to that of a 25 per cent resin solution may be obtained by increasing the concentration of alkali to 12 to 15 per cent on the weight of the resin. Similar solutions may be prepared by the use of sodium carbonate in concentrations which provide a Na_2O content equivalent

to the stated proportions of sodium hydroxide. Films obtained from aqueous accroides solutions are improved by the inclusion of butyl Carbitol as a plasticizer.

Solutions for Paper Sizing and Stiffening Fiber Board. Aqueous alkaline solutions of the manilas or of accroides are suitable for paper sizes and for stiffening fiber board. For either use, the resin must be capable of being precipitated from the solution by addition of an acid. For stiffening fiber board, it is also desirable that the resin have some thermosetting properties.

The size solution is added to the pulp in the beater as are the various fillers, coloring materials, etc. In subsequent processing, the paper or fiber board undergoes drying and pressing operations between steam-heated steel drums, calenders, or platen presses. The heat-reactive properties and cheapness of accroides make this resin particularly suitable for fiber board. The color of its solution is not satisfactory for the majority of paper products. Manila solutions are more satisfactory.

Resin acids which have been precipitated from a sodium hydroxide solution of the resin dissolve readily in ammonia and borax solution. These sizes are about as water- and wear-resistant as shellac size and also fix basic dyes as well. If Manila resin acids in alkali solutions be treated with 0.5 gram equivalent of sodium hypochlorite per 100 grams of resin, and then precipitated with mineral acid, the product gives a nearly colorless size. The viscosity may be decreased by the addition of butyl Carbitol, which also improves the flexibility of thick coatings.

Manila Dispersions as Intaglio Ink Vehicles. Manila dispersions containing sulfonated castor oil serve as the vehicle for non-inflammable, non-toxic intaglio inks for high-speed printing.

Formula 531—Manila Intaglio Ink Vehicle

Solution I

- 400 lb. manila DBB
- 400 lb. (59 gal.) denatured ethyl alcohol
- 100 lb. (12.7 gal.) sulfonated castor oil

Solution II

- 400 lb. triethanolamine
- 1,000 lb. (120 gal.) water

Solution III

- 300 lb. (38.1 gal.) sulfonated castor oil
- 1,200 lb. (144 gal.) water

and

- 60 lb. (7.9 gal.) ammonium hydroxide (specific gravity 0.910)

Procedure: Prepare solution I by dissolving the sulfonated castor oil in the alcohol and then stirring in the ground resin. Heat to 60°C. and add the ammonium hydroxide with high-speed stirring. The temperature will drop to about 50°C. Preheat solution II to 50°C. and add it to solution I, using high-speed stirring. When the mixture has cooled somewhat, add solution III with continued high-speed stirring.

Methods of Emulsification and Dispersion of Resin in Water. Natural resin varnish bases may be emulsified and water incorporated as a thinner by the use of materials like triethanolamine, morpholine, and fatty acid esters. For applications as a varnish, the water should be the inner phase, that is, dispersed in the varnish base. When the emulsion is brushed out, the water evaporates in the same manner as an organic solvent, leaving colorless, transparent films. Before emulsification, driers or pigments may be incorporated. Commonly a quantity of water equal to the varnish base so that the resulting material is 50 per cent water may be added. Emulsifying agents such as the sulfonated oils, the sulfonates of the fatty acid alcohols, or the substituted sulfonic acids are usually not satisfactory for varnish-type emulsions.

In another modification where the resin or the varnish base is dispersed in water, a range of emulsifying agents may be employed, but here again the fatty acid esters of triethanolamine and morpholine are more satisfactory than other types.

The ordinary procedure for the use of these emulsifying agents involves solution of the morpholine or triethanolamine in the desired amount of water, dissolving the acid in the other constituent and mixing the two in a manner determined by the type of product desired. Several variations of this method are possible. As an example, consider the emulsification of a solvent solution of damar or damar wax. Such a solution containing 50 per cent of the resin in mineral spirits may be made and to it 2 per cent of its weight of morpholine and 2.2 per cent of its weight of oleic acid added, stirring until a homogeneous solution is obtained. Under continued stirring, water is added in small quantities at a time. After each addition of water, stirring is continued until the water has all been taken up before the next addition is made. At first, the mixture, a white liquid, retains the viscosity of the original solution. After a certain amount of water has been added (a quantity to be determined by experimentation), the viscosity may change suddenly from that of a rather viscous liquid to one of water-like consistency. This change is due to a reversion of the emulsion from the water-in-oil type to the oil-in-water type. These two types have their own specific fields of application.

No mention is made of optimum temperatures. Where a liquid is to be emulsified, operation may be at room temperature, provided the liquid is not too viscous. The resins in combination with waxes, stearic acid, and similar materials present a different situation. Dispersion is desired of a material which is solid at ordinary temperatures. It is necessary to heat both water and mixture until the latter is sufficiently liquid, before combining them.

An interesting application is found in the resin-wax mixtures in the same manner that the so-called soluble oils, or the soluble waxes, are used. These may be emulsified without emulsifying agents. Twenty-five parts of a mixture containing equal parts of Batavia damar A/D and beeswax are melted, then 1 part of morpholine and 1.5 parts of stearic acid incorporated. This product is allowed to cool to room temperature. A homogeneous solid is obtained which may be kept indefinitely. To produce an emulsion, the material is melted and stirred into water at the same temperature. A temperature of 90°C. is suggested.

"Liquid wax" polishes are a field for resin emulsions. Two types are prepared, the "dry-bright" or "no-rub" polishes, and polishes which require rubbing to produce luster. Damar, the manilas, pale east india, and run congo may be incorporated in satisfactory formulations.

With resin-wax combinations of sufficiently low melting point, the resin-wax mixture may be liquefied and the emulsion formed by ordinary methods. If the melting point of the mixture be such, however, that the addition of water, even at the boiling point, will cause the melted compound to solidify, other methods for obtaining a satisfactory dispersion must be employed. The manilas may be incorporated as aqueous alkaline solution by mixing with a previously prepared wax emulsion. A typical formulation for a "no-rub" polish containing manila would be:

Formula 532—"No-rub" Emulsion Polish

Carnauba wax emulsion

- 30 lb. carnauba wax No. 1 yellow
- 210 lb. (25.2 gal.) water
- 3 lb. triethanolamine
- 5 lb. oleic acid

Manila solution

- 30 lb. manila DBB
- 158 lb. (19 gal.) water
- 12 lb. ammonium hydroxide (28 to 29 per cent NH_3)

Finished polish

- 34 lb. carnauba wax emulsion
- 39 lb. manila solution

The carnauba wax emulsion is prepared by melting the wax together with the oleic acid in a steam-jacketed vessel or boiling water bath. When the mixture becomes homogeneous the triethanolamine is incorporated. Boiling water is added in small portions, the mixture being well agitated after each addition. During addition of the water the emulsion passes through three stages. It gradually thickens to a gel-like form which later reduces to that of a heavy cream. Upon further addition of water the creamy mixture suddenly breaks to a watery consistency as the emulsion inverts. Prior to this inversion it is important that the addition of water be made carefully so that a homogeneous mass is obtained. Too slow or too rapid addition of the water will result in a poor dispersion.

The manila solution is prepared by agitating the finely powdered resin in the ammonia solution until dissolved and then straining to remove insoluble matter. The resin solution is added to the carnauba wax emulsion, after cooling, and stirred. The emulsion polish gives glossy, waterproof films.

Similar emulsions may be prepared using sodium hydroxide in the preparation of the resin solution. Since the sodium-resin soap formed is retained in the film, the product shows a decreased water resistance and is not suitable for application over surfaces easily attacked by alkali. If the odor of the ammonia prove objectionable, a volatile amine may be substituted.

Improved film characteristics may frequently be obtained by the inclusion of small amounts of borax solution which should be added to the triethanolamine-oleic acid-wax mixture just before addition of the boiling water. The borax solution should be at the boiling point. The borax permits a more rapid addition of water, and the rapid introduction of boiling water usually results in films of improved gloss. The emulsions may be used for polishing floors, furniture, and metal surfaces.

No-rub polishes (Table CXXI) may be prepared from run congo in the following manner: The wax is melted and the ground congo added at about 125 to 150°C. The mixture is held at this temperature until homogeneous and then placed in a boiling water bath. The oleic acid is added slowly with vigorous stirring and the triethanolamine is then added in the same manner. The sodium hydroxide is dissolved in 25 parts of water, heated to boiling, and slowly added to the mixture with vigorous stirring. The remainder of the water, heated to the boiling point, is added to the homogeneous mixture with vigorous stirring. The polish dries quickly to a hard, glossy, waterproof film.

TABLE CXXI*

	Emulsion Polishes No-Rub	Emulsion Polishes Floor	Cloth Stiffeners	
Formula No.	533	534	535	536
Carnauba wax	30	30	...	...
Thermally processed congo	30	...	...	...
Pale east india	...	30	...	...
Damar A/D	...	...	10	5
Stearic acid	...	...	10	...
Paraffin	...	...	...	5
Sodium hydroxide	0.5	0.5	...	...
Morpholine	...	...	1	1
Triethanolamine	4	4	...	...
Oleic acid	9	9	...	2
Water	420	420	100	100

* All quantities in pounds.

An emulsion suitable for use as a floor polish (Table CXXI) to be rubbed to high luster may be prepared from pale east india resin in a manner similar to that of the preceding congo formulation. For both, agitation is continued during cooling of the emulsion. The polish is a cream-colored liquid of the oil-in-water type. It should be applied in thin films, permitted to dry, and rubbed to a gloss.

Emulsions of damar with wax may be used as impregnating media for stiffening cloth. Two typical formulae for stiffening cotton are given in Table CXXI. The formula 535 is prepared as follows: The damar and stearic acid are melted, brought to a temperature of 90 to 95°C., and morpholine added with stirring. The water, which has been preheated to 90 to 95°C., is then added.

In another formula (536) paraffin is melted and the pulverized damar gradually added with stirring while the temperature is maintained at about 125°C. The mixture is permitted to cool to 90 or 95°C. and oleic acid and morpholine added in that order with agitation. The water, preheated to 90 to 95°C., is then added slowly with agitation. Cloth impregnated with either of these emulsions should be dried at 210°F.

Pigmented damar emulsions may be used as white shoe cleaners. Various methods of preparation may be employed and fluids which exert a cleansing action may be included if desired. Typical formulations are given in Table CXXII.

TABLE CXXII

WHITE SHOE CLEANERS

Formula No.	537		538*	
	lb.	gal.	lb.	gal.
Titanium-barium pigment (30% TiO_2)	240	...	...	...
Titanium dioxide	...	...	5	...
Lithopone	...	...	15	...
Batavia damar A/E	20	...	4	...
Petroleum naphtha	110	18	13	2.13
Carbon tetrachloride	...	...	10	0.75
Triethanolamine stearate	10	...	2	...
Water	100	12	51	6.1

* C. F. Mason, *Chem. Ind.*, **44**, 533–4 (1939).

In formula 537 the damar is dissolved in the petroleum naphtha and filtered to remove insolubles. The triethanolamine is then dissolved in hot water and the pigment slowly added with high-speed agitation. When a smooth paste has been obtained the damar solution is slowly added. At the start of the addition, the pigment drops out and shows a reluctance to mix, but on further addition, a smooth, thin paste will result.

Mason[1] dissolved damar in the petroleum naphtha and filtered to remove insolubles. The triethanolamine stearate is dissolved in warm water and the solution permitted to cool. The resin solution is then added to the water solution slowly and with vigorous agitation. When a smooth emulsion has been obtained, the carbon tetrachloride is stirred in, followed by the pigments.

Formula 539—Copal Oil Emulsion

500 lb. copal oil
2,000 lb. (240 gal.) water
20 lb. morpholine
45 lb. oleic acid

Procedure: The oleic acid, morpholine, and water, in the order given, are added slowly to the copal oil with continuous rapid agitation. The emulsion yields sticky films which may possess possibilities as a base for the preparation of tree lacs or adhesives.

[1] *Chem. Ind.*, **44**, 533-4 (1939).

Emulsified combinations of damar and elemi may be added to rubber-latex dispersions.

Formula 540—Damar-Elemi Emulsion

130 lb. elemi
15 lb. damar
6 lb. triethanolamine
17 lb. oleic acid
256 lb. water
3 lb. triethanolamine

The elemi and oleic acid are heated together until a homogeneous liquid is obtained. The temperature is then raised to 125°C. and the pulverized damar added. When the mixture has cooled to 100°C. the triethanolamine is stirred in and the mixture allowed to cool to 90 to 95°C. The preheated solution of triethanolamine in water is then slowly added with agitation. Stirring is continued during cooling of the emulsion. The final product is of water-like consistency. Twenty-five per cent of a latex dispersion of approximately the same solids content (36 to 39 per cent) may be added to this emulsion. The product is a white emulsion of approximately the same viscosity as the latex dispersion used. Films obtained are clear and sticky, possessing good properties as adhesives. If appreciably higher percentages (50 to 75 per cent) of latex are used, gelation of the emulsion occurs.

Aqueous manila dispersions may be added to latex solutions in limited amounts. Satisfactory emulsions and films are obtained with 25 per cent or less of manila solution. The inclusion of manila tends to harden and strengthen the film. Concentrations of the order of 50 per cent cause thickening to a gel-like consistency. Use of aqueous accroides solutions causes either gelation or precipitation of the latex.

The examples given in this chapter are intended to be only illustrative. Various other resins, waxes, and waxlike materials may be used in the procedures described.

CHAPTER XXIV

MISCELLANEOUS APPLICATIONS

Adhesives. Natural resins and their solutions find many applications in the preparation of adhesives and cements for a variety of purposes.

Elemi may be combined with castor oil to yield light-colored adhesives having a wide range of tackiness and consistency. Such materials have been prepared in proportions varying from 2 to 20 per cent castor oil. Small amounts of castor oil produce a stiff tackiness whereas increased percentages give softer body and more stringy adhesives. These compositions retain their tackiness and may be used in the manufacture of adhesive tapes. They are prepared by melting the ingredients together at the lowest temperature affording a homogeneous mixture. The high essential oil content of elemi gives water-repellent properties.

With low percentages of castor oil, addition of damar in ratios between 2.5 and 7.5 parts to 1 of castor oil produces adhesives of increased viscosity which retain their stickiness. Damar in low percentages provides adhesives which will cause paper to adhere to painted surfaces but at a later date the paper may be removed in a manner similar to Scotch tape (formula 541).

If an adhesive having the same properties but a heavier body is desired, the damar content may be increased to 5 parts. When still larger amounts of damar are used, the paper cannot be removed in the manner of Scotch tape (formula 542).

Substitution of manila for damar in ratios between 5 and 7 parts to 1 of castor oil gives stiff, tacky adhesives which dry and become brittle. Inclusion of either damar or manila tends toward more rapid drying.

Similar light-colored adhesives may be prepared, with light vegetable pitch in concentrations of $\frac{1}{4}$ to 2 per cent replacing the castor oil. Proportions below 1 per cent produce adhesives which dry when exposed in films. With larger amounts the adhesives are less viscous and the films retain their tackiness. Inclusion of damar or manila in ratios between 5 and 7 parts to 1 of pitch produces adhesives the films of which possess only slight tackiness and when dry become brittle. In

TABLE CXXIII*

Formula No.	541	542	543	544	545	546
Manila WS	...	...	...	...	150	...
Elemi	49	49	...	4	5	...
Batavia damar A/E	2.5	7.5	...	...	...	20
Rosin	...	...	7.5	6	...	...
Thermally processed congo	...	...	2.5	...	...	...
Ethyl cellulose (L.V.)	...	...	...	...	...	10
Paraffin	...	...	...	...	...	2
Denatured ethyl alcohol	...	...	...	...	100	14
Acetone	...	...	...	...	55	...
Toluol	...	...	...	...	...	54
Castor oil	1	1	...	...	...	...
Dry color	...	...	0.5	0.5	...	...

*All quantities in pounds.

applications such as black rubber adhesive tapes, combinations of elemi with asphaltic materials may be used.

Adhesives useful to optical houses may be prepared from run congo. These are used to attach lenses to a steel grinding block and must be resistant to the heat generated by grinding. Run congo alone does not provide suitable adhesion to glass and is therefore used in combination with rosin or elemi. Formulations 543 and 544 have good adhesion to glass and are not greatly affected by heat.

For attaching labels to tin cans cold adhesives, consisting of manila solutions plasticized with elemi, may be prepared as in 545 (Table CXXIII). The back of the label is coated with a thin film of adhesive and applied immediately to the can. The solids content of the adhesive is 50 per cent.

In applying labels to cartons light-colored thermal adhesives containing damar and ethyl cellulose may be used. Formulation 546 (Table CXXIII) has been found to give good results. The ingredients are agitated together until solution is complete and then centrifuged to remove suspended matter. The solution is slightly turbid. It has a Gardner-Holdt viscosity of P and a color of 6 on the Gardner color standards. A small quantity of paraffin has been included to prevent excessive penetration and, upon standing, separation of a portion of the wax may take place. The separated material may be easily reincorporated by agitation.

The method of application is to coat the back of the label with the

adhesive and permit it to dry thoroughly. The treated surface is then placed against the carton and a hot iron (approximately 265°F.) is passed over the face of the label. The label will adhere firmly to the carton. The formulation as given is unplasticized and becomes somewhat brittle upon standing. This brittleness does not impair the adhesive qualities of the material. If flexibility is required, the adhesive may be plasticized using 10 per cent, based upon total solids, of a plasticizer such as hydrogenated methyl abietate. Adhesives of the thermal type are also used in mounting photographs.

Solutions of damar, batu, and the east indias in aromatic hydrocarbons or high-solvency petroleum thinners may be added to solutions of crepe rubber to provide pressure cements of improved bonding characteristics. Formulations are given in Table CXXIV.

TABLE CXXIV

PRESSURE ADHESIVES

Formula No.	547		548	
	lb.	gal.	lb.	gal.
20% Crepe rubber solution in benzol	71	...	71	...
Batavia damar A/E	11	...	...	...
Pale east india nubs	...	...	10	...
Benzol	11	1.51	...	...
Toluol	...	...	19	2.64
Mineral oil	7	...	...	...

Damar provides light-colored adhesives of lower bonding strength than those obtained from batu and the east indias. The batu and east india cements are adapted to the bonding of leather, wood, and cloth. Table CXXV shows typical formulations for linoleum adhesives. The resin solution is prepared by agitation and the fuller's earth then stirred in to form a paste. The consistency of the paste may be altered by varying the proportion of fuller's earth. Concentrations between 30 and 40 per cent have been found to be satisfactory. The solvent may be replaced by a straight-run petroleum thinner to which about 15 per cent of a coal-tar solvent has been added. The batu nubs and chips may be replaced by any of the east india grades. Similar cements may also be prepared with manilas (formula 550).

East india and manila solutions of this type, but without fillers, are

TABLE CXXV

LINOLEUM ADHESIVES

Formula No.	549		550	
	lb.	gal.	lb.	gal.
Batu nubs and chips	35	...	...	...
Manila DBB	...	...	30	...
High solvency petroleum naphtha	35	5.73	15	2.45
Denatured ethyl alcohol	...	...	15	2.28
Fuller's earth (through 200 mesh)	30	...	40	...

used as gasket cements. For adhesives resistant to chemical action the East India resins are satisfactory.

Resin-Wax Mixtures and Polishes. Natural resin-wax combinations have been studied by Allan,[1] who reported the combining temperature, loss in weight, and melting point for various natural resins combined with carnauba wax (No. 1 yellow), Japan wax (Chickusan), montan wax (crude), ozokerite (natural yellow), beeswax (pure crude), and paraffin wax. The resin-wax combination was prepared by melting the wax in a tared beaker and slowly adding an equal weight of resin. The mixture was agitated until homogeneous. The combining temperature and weight of beaker and contents were recorded and the mixture cast in metal trays. When cool, melting points were determined by the mercury method. Melting points of the original materials are given in Table CXXVI. Detailed results obtained in producing the different mixtures are given in Table CXXVII.

In certain cases it was necessary to raise the temperature to the range of "running" in order to dissolve the resin in the wax within a reasonable length of time. Solution may be attained at lower temperatures if greater lengths of time are employed.

Natural resins dissolve in waxes with varying degrees of ease. The damars and east indias and also elemi dissolve in the waxes without being run or at least partially run. The loss of weight is an indication of the relative ease with which solution takes place. Manila-, congo-, and kauri-wax mixtures lose much more weight in the process of combination than do the corresponding damar mixtures.

A resin difficultly soluble in wax may be combined by a mutual sol-

[1] R. W. Allan, *Chem. Ind.*, 42, 507 (1938).

TABLE CXXVI

MELTING POINTS

Resins	Melting Point, °C.
Batavia damar B	96–100
Singapore damar No. 2	114
Black east india bold scraped	160–164
Batu scraped	168–180
Pale east india Macassar bold	127–156
Pale east india Singapore bold	147–156
Manila MA	121
Loba C	114–123
Congo No. 4	178
Congo No. 11	193–200
Kauri pale No. 1	128
Run brown kauri No. 2	120–130
Elemi	Plastic
Waxes	
Beeswax (pure crude)	61.5
Carnauba (No. 1 yellow)	80
Japan (Chickusan)	43
Montan (crude)	68
Ozokerite (natural yellow)	49
Paraffin	49

vent without marked loss in weight. Elemi is easily soluble in waxes whereas loba C is not. Loba C is easily soluble in elemi. Elemi may be considered a common solvent for the waxes and the resin and become a medium to effect their combination. Manila resins may be dissolved in melted elemi and carnauba added to form a ternary mixture in which both resin and wax are stable.

With the exception of elemi, addition of a resin to wax usually raises its melting point. Elemi, while lowering the melting point, acts as a plasticizer. Solid resin-wax combinations such as those obtained with damar and the east indias are marketed in pulverized form as waxes for dance floors. Similar materials are used to coat shipping containers.

Pale east india is utilized with various waxes in the preparation of wax-solvent type polishes. Four typical formulations are listed in Table CXXVIII. These polishes are prepared by melting the waxes, adding the resin, and combining the two at 150°C. After cooling to 130 or 140°C. the solvents are added, the mixture stirred until homogeneous and then permitted to cool to room temperature.

Formulations 552 and 554 give the greatest consistency. Number 551 has the consistency of butter whereas 553 is liquid at room temperature with pasty particles precipitated from it. The polishes are ap-

TABLE CXXVII

DATA ON RESIN-WAX MIXTURES

Mixture	Combining Tempera-ture, °C.	Loss in Weight, per cent	Melting Point, °C.
Batavia damar B and beeswax	90–100	0.4	59.5
Batavia damar B and carnauba	90–100	1.0	66
Batavia damar B and Japan	90–100	0.0	47
Batavia damar B and montan	90–100	0.4	76
Batavia damar B and ozokerite	90–100	0.0	64
Batavia damar B and paraffin	140–150	0.5	49
Black east india bold scraped and beeswax	130–140	0.6	65
Black east india bold scraped and carnauba	130–140	2.0	82.5
Black east india bold scraped and Japan	130–140	1.2	75
Black east india bold scraped and montan	130–140	0.4	99
Black east india bold scraped and ozokerite	130–140	0.0	73
Black east india bold scraped and paraffin	130–140	...	62
Pale east india Macassar bold and beeswax	120–130	0.4	62.5
Pale east india Macassar bold and carnauba	120–130	1.4	75
Pale east india Macassar bold and Japan	120–130	1.0	65.5
Pale east india Macassar bold and montan	120–130	0.8	83
Pale east india Macassar bold and ozokerite	120–130	0.2	77
Pale east india Macassar bold and paraffin	150–200	...	55
Pale east india Singapore bold and beeswax	120–130	1.2	62
Pale east india Singapore bold and carnauba	120–130	1.8	76
Pale east india Singapore bold and Japan	120–130	0.2	80
Pale east india Singapore bold and montan	120–130	0.6	95
Pale east india Singapore bold and ozokerite	120–130	0.0	86
Pale east india Singapore bold and paraffin	150–200	...	64
Elemi and beeswax	98–100	...	56.5
Elemi and carnauba	100	1.0	57
Elemi and Japan	98–100	1.0	45.5
Elemi and montan	100	1.2	60.5
Elemi and ozokerite	100	1.0	70
Batu bold scraped and beeswax	130–140	0.0	65
Batu bold scraped and carnauba	150–200	2.2	85
Batu bold scraped and Japan	150–200	2.6	75
Batu bold scraped and montan	150–200	2.0	127
Batu bold scraped and ozokerite	150–200	2.8	74
Batu bold scraped and paraffin	150–200	...	69.5
Singapore damar No. 2 and beeswax	100–110	2.6	60
Singapore damar No. 2 and carnauba	110–120	0.8	79.5
Singapore damar No. 2 and Japan	90–100	0.0	42
Singapore damar No. 2 and montan	90–100	0.0	75
Singapore damar No. 2 and ozokerite	130–140	0.0	67
Singapore damar No. 2 and paraffin	140–150	0.5	50
Manila WS and beeswax	275–325	18.2	69
Manila WS and carnauba	275–325	16.4	80
Manila loba C and beeswax	300–325	26.3	68
Manila loba C and carnauba	300–325	17.0	79
Congo No. 4 and beeswax	300–325	18.5	66
Congo No. 11 and beeswax	300–325	17.6	68
Congo No. 11 and carnauba	300–325	21.8	75.5
Kauri pale No. 1 and beeswax	300–325	14.3	67
Kauri pale No. 1 and carnauba	300–325	10.0	81.5
Run brown kauri No. 2 and paraffin	300–325	...	54

TABLE CXXVIII*

Formula No.	551	552	553	554
Pale east india Macassar bold	18	16	14	15
Paraffin	8	15	...	14
Carnauba wax	6	14	13	13
Turpentine	68	...	6	29
V. M. and P. naphtha	...	65	56	29
Montan wax	...	...	5	...
Beeswax	...	...	4	...
Pine oil	...	...	2	...

* All quantities in pounds.

plied in small quantities with a dry rag and rubbed until dry. They are quick drying and give hard, glossy films. Such polishes are primarily designed for floors or automobiles.

The East India resins may be combined with petrolatum stock waxes in formulations for waterproofing compounds. Paraffin is added to reduce the cost and improve the characteristics of the compound. The petrolatum waxes are made from petrolatum stock obtained in the refining of petroleum. They are light in color, tough, flexible, and of an amorphous or possibly micro-crystalline structure. They have high melting points (160 to 170°F.) and retain their flexibility at low temperatures. They also retain their consistency without loss of volatile oils at temperatures as high as 130°F.

Waterproofing compositions may be prepared from materials in the following proportions:

Formula 555

Petrolatum wax	45 per cent
East india resin	45 per cent
Paraffin	10 per cent

Procedure: The waxes are melted and the ground resin added. The mixture is stirred until homogeneous. Results obtained with batu and pale and black east india are compared with those of ester gum in Table CXXIX.

The east india formulations show better water resistance than the ester gum compound but are less flexible, darker in color, and show greater weight losses during preparation. These differences in properties may be attributed to the higher combining temperature (200 to 225°C.)

TABLE CXXIX

No.	Resin	Per Cent Loss on Combining	Melting Point of Mixture, °C. Mercury Method	Condition of Panel after Immersion for One Week
1	Ester gum	0.3	58	Definite loss of gloss
2	Pale east india Singapore chips	4.7	65.5	No visible change
3	Bold black scraped	4.4	69	No visible change
4	Batu bold scraped	4.0	69	No visible change

Pyrotechnics. Natural resins enter the manufacture of fireworks. In solution they serve as the binding medium for the various constituents. When pulverized, the resin becomes one of the active combustible ingredients.

Molded Plastics. The natural resins are ordinarily considered to be varnish resins rather than raw materials for molded plastics. Dewaxed damar has been used in the preparation of injection molded ethyl cellulose plastics and was found to impart excellent molding characteristics. Damar has also been employed in the preparation of molded objects from urea-formaldehyde resins. A large proportion of the unpurified damar wax, which is a by-product of the lacquer industry, is consumed as a cheap filler in the manufacture of dark-colored molded articles. Broader opportunities in molded plastics are to be found in modifications wherein the natural resin has been chemically combined with other materials to form a synthetic resin.

Moisture-Proof Coatings for Cellophane. Natural resins may be included as an ingredient of lacquer-type surface coatings for application to transparent regenerated cellulose sheets. The product is the transparent, moisture-proof, heat-sealable wrapping material known as moisture-proof cellophane. Examples of *N*-alicyclic aryl sulfonamides as plasticizing materials for such compositions[2] are given in Table CXXX.

"Solvent" designates suitable solvent mixtures such as esters, alcohols, and hydrocarbons. Kauri and sandarac as well as other cellulose derivatives may be substituted.

[2] E. F. Izard and J. A. Mitchell (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,192,314 (March 5, 1940).

TABLE CXXX*

Formula No.	556	557
Cellulose nitrate	26.9	12
Dewaxed damar	6.6	3
Wax	1.9	...
N-Decahydronaphthyl *p*-toluene sulfonamide	...	4
Cyclohexyl *p*-toluene sulfonamide	14.1	...
Castor oil	2.6	...
Solvent	353.5	166

* Parts by weight.

Linoleum.[3] Linoleum is the work of an English inventor, Frederick Walton, who in 1860, while attempting to produce artificial leather, experimented with various methods of treating linseed oil. His attention was attracted to the tough skin that formed on the surface of some of his tubs of oil, caused by exposure to the oxidizing effects of the air. He experimented with various compounds of oxidized linseed oil and found that when combined at high temperatures with natural resins, and mixed with finely ground cork and color pigments, the oil produced a plastic which, when rolled onto a fabric and dried, made a durable, sanitary floor covering. He named the product linoleum, from the Latin words *linum* (flax) and *oleum* (oil).

The natural resin with which Walton perfected the composition was kauri (together with rosin), and for many years kauri predominated as the resinous constituent employed in its production. Modern linoleum manufacture utilizes a variety of resins, both natural and synthetic, singly and in combination. Of the naturals, the inexpensive east indias have met with favor in this country while the dust grade of congo has been employed abroad. Manilas have also found some use in this field.

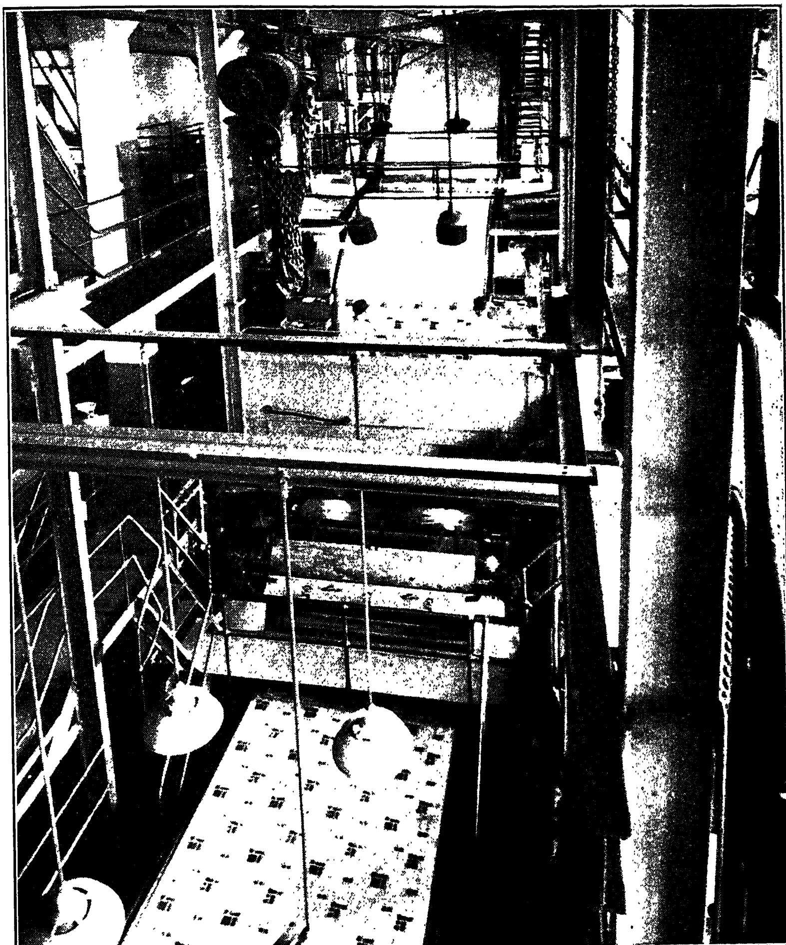
Not content with linoleum of plain color, Walton continued to experiment with various methods of producing color variegations and designs. Finally, in 1904, he perfected and patented a successful automatic straight line inlaying machine (Fig. 75). Prior to his death in 1928, he had seen several of these gigantic machines erected in Great Britain and the United States.

Linoleum manufacture starts with the heat-refining and oxidizing

[3] The information on linoleum is due to the courtesy of R. D. Bonney, Assistant Manager of Manufacturing of Congoleum-Nairn, Inc.

of linseed oil. The refined oil is oxidized to convert the liquid into a yellowish, rubbery solid.

In one method the oil is run down over long sheets of cotton cloth which are suspended in a high building. The sheets are coated in this



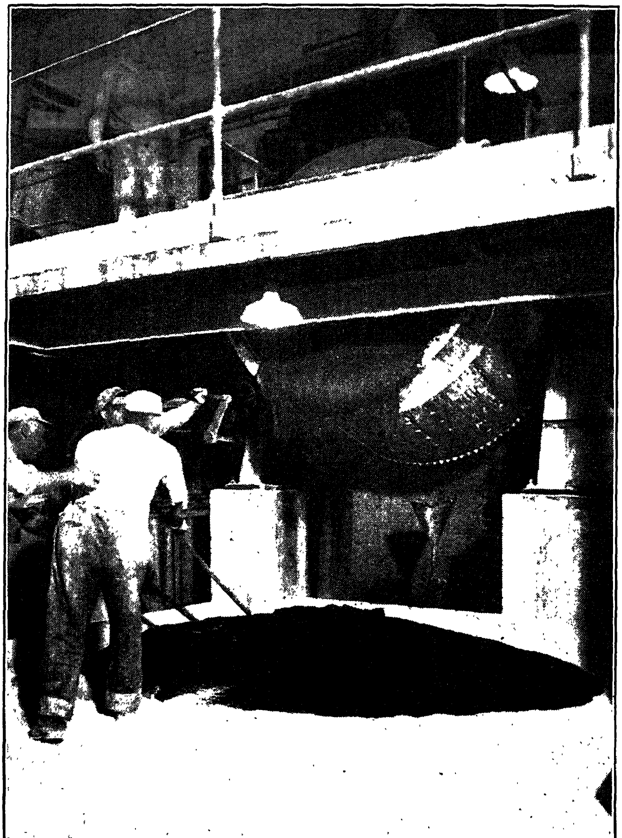
Courtesy Congoleum-Nairn, Inc.

FIG. 75. Straight line linoleum inlaying machine.

way each day for several months and, as each layer dries, the sheets or "skins" become thicker, finally reaching a thickness of ½ to ¾ inch. The "skins" are then cut down and the solid oil ground into fine "bread-crumb" condition.

The second method—mechanical oxidation—is accomplished by passing air through the oil while it is heated and agitated in closed cylinders, until it solidifies to a jelly-like mass.

Linoleum cement, the tough ingredient which binds all the constituents of linoleum into a plastic mass, is made by fusing the two types



Courtesy Congoleum-Nairn, Inc.

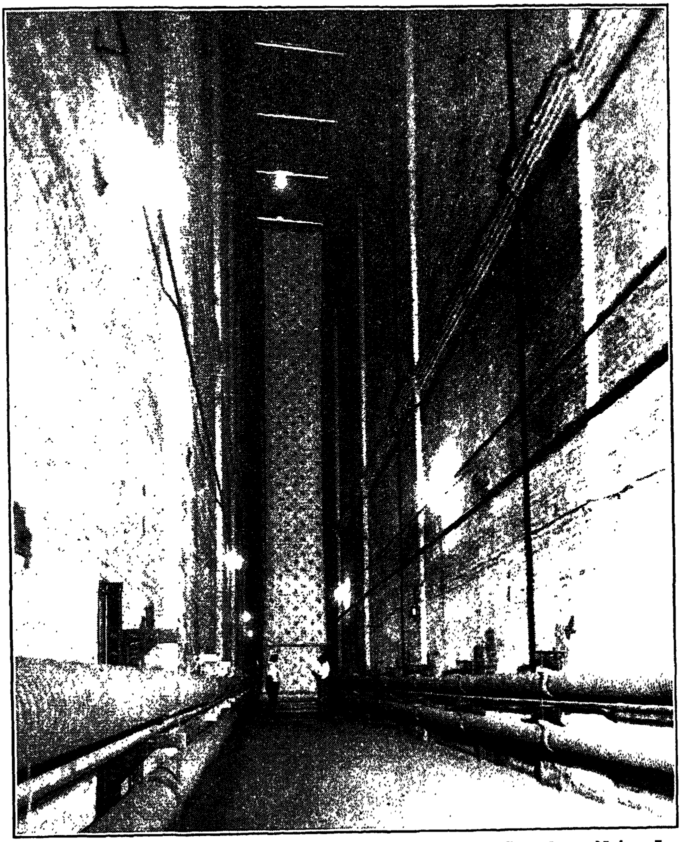
FIG. 76. Cement kettles.

of oxidized oil, in proper proportions, with resins (Fig. 76). It is allowed to age several weeks before use.

The aged cement, ground cork, wood flour, and coloring pigments are then introduced into a system of massive mixers, where they are combined into a plastic mass called linoleum composition.

Battleship and plain linoleum are produced by feeding linoleum

composition in granular form between heated calender rolls, weighing several tons, which form it into a sheet and key it to a backing fabric. Jaspé or grained effects are obtained by feeding granules of two or more differently colored compositions.



Courtesy Congoleum-Nairn, Inc.

FIG. 77. Linoleum seasoning oven.

In making straight-line inlaid linoleum, sheets of each of the plain or marbleized colors in the pattern are produced by calender rolls. Each sheet is then led to an individual cutting cylinder on the rotary inlaying machine. Simultaneously a prepared backing fabric enters the machine, carried on the surface of a large drum. The backing fabric may be any one of several suitable materials such as burlap, cotton, or asphalt-saturated felt.

Each sheet of linoleum is cut into figures or blocks of the proper size and shape by the cutting cylinder, the surface of which is covered with knives or dies. These dies are so operated that the various figures which are to appear in the finished pattern are automatically placed on the backing fabric as it is carried around the drum.

Finally the backing, carrying the linoleum inlays, passes through a finishing press which welds the figures together, binds them firmly to the backing, and gives a smooth, lustrous surface.

Seasoning, necessary to harden the composition, is accomplished in huge ovens, where the linoleum is hung in long loops or festoons and baked at closely regulated temperatures (Fig. 77). Weeks are required for this process, which continues until the linoleum passes established tests for firmness, resilience, and toughness.

After the linoleum is seasoned it is given a finishing treatment, usually including wax coating.

The final step is examining and packing. The examination takes place on long tables, where special lighting equipment makes discernible any defect. Defective material is rejected. After being examined, the linoleum is wound into standard size rolls, packed, and delivered for warehousing or shipment.

Fritz[4] studied copal dust for linoleum manufacture. Cleaning the better grades of copal leaves large quantities of copal dust for disposal. Copal dust, without preliminary treatment, does not fuse with linseed oil to a homogeneous mass. The mass contains small, solid pieces of copal, which leave spots in the linoleum made therefrom. Copal dust can be fused at 300°C. and kept at this temperature until a sample removed becomes soluble in hot linseed oil, when it is poured into shallow metal boxes to harden. The loss is about 31 per cent, with only slight darkening. The cooled copal can be used with linoxyn in the manufacture of linoleum.

[4] F. Fritz, *Nitrocellulose,* **10**, 63-4 (1939).

CHAPTER XXV

DETECTION AND IDENTIFICATION

The identification of unknown resin samples and the detection and estimation of resinous materials in the many products comprising their commercial applications have received much attention from chemists and technologists over a period of many years. Several types of procedure have been developed, most of which have been subjected to numerous modifications. The methods may be classified as identification by

1. Color reactions.
2. Chemical and physical constants.
3. Determination of the resin constituents.
4. Fluorescence analysis.
5. Capillary analysis.
6. Microscopical examination.

Unfortunately, however, the literature abounds with references questioning the reliability of the results obtainable by these methods. This is true in the procedures involving color reactions, inasmuch as rosin, shellac, and the natural resins all possess constituents which are closely related and which in many instances are transformed into allied substances. The oils, waxes, and other components in surface coatings often contain acids or esters similar to those of the resinous constituents. The synthetic resins produced for surface-coating applications usually contain large amounts of rosin, ester gum, or esterified copal. The compounds used in the preparation of synthetic resins frequently possess a variety of characteristic color reactions.

The Liebermann Test. Of the color reactions used for the identification of resins, that of Liebermann,[1] subsequently modified by Storch[2] and then by Morawski,[3] is probably best known. The test is referred to by a number of names, such as Liebermann-Storch, Storch-Morawski, Storch-Morawski (Liebermann), etc. It, as well as its modifications, consists of dissolving the resin in boiling acetic anhydride and, after

[1] *Ber.*, **17**, 1884 (1884).
[2] *Ber. osteri. Ges. chem. Ind.*, **9**, 93 (1887).
[3] *Chem.-Ztg.*, **12**, 1321 (1888).

cooling to room temperature, observing the color developed upon addition of sulfuric acid.

The Liebermann test was developed specifically as a test for rosin. A modification proposed by Burchard,[4] in which he used chloroform as an inert solvent, has apparently met with little favor. Wolff[5] reported that the Storch-Morawski test using glacial acetic acid and one drop of sulfuric acid, when conducted upon oil varnishes containing rosin, gave a red coloration which later turned blue, green, etc. Other natural resins, synthetic resins, and poorly purified oil gave the same reaction, whereas aged rosin gave negative results. Wolff also made an investigation of sandarac[6] and reported the results of the Storch-Morawski test upon eighteen samples. Stock[7] criticized the rejection of positively reacting Albertol varnishes.

Schulz and Krämer[8] stated that if the positive Storch-Morawski test be designated as the immediate formation of a violet coloration at least as deep as that of a 0.001 *N* solution of potassium permanganate, with a subsequent rapid change to dirty browns or green colors, the test was found to be specific for rosin. Oxidized rosin did not respond as specified and phytosterol and hydroxy fatty acids gave results similar to rosin but of longer duration. Wolff[9] discussed the work of Schulz and Krämer and pointed out some of the limitations of the Storch-Morawski reaction. The reaction was reviewed by Marini.[10] Donath[11] cited the interference of cholesterol (wool fat) and of cellulose which gives colored decomposition products with sulfuric acid.

Michel[12] proposed the following modification. Dissolve the test sample in 3 cc. of chloroform, add 5 cc. of 65 to 67 per cent sulfuric acid and shake strongly. With 3 mg. or more of rosin, a yellow color appears in the sulfuric acid layer. Fractions of a milligram of rosin produce a violet coloration in the chloroform layer upon dropwise addition of acetic anhydride. When shaken, the sulfuric acid layer assumes a purple-red to carmine-red color. Repetition until acetic anhydride no longer affects the chloroform layer gives a coloration in the sulfuric acid

[4] Burchard, Dissertation, Rostock, 1889.
[5] H. Wolff, *Farbe u. Lack,* 605-6, 1926.
[6] H. Wolff, *Farben-Ztg.,* **31,** 1682 (1926).
[7] E. Stock, *Farben-Ztg.,* **31,** 2777 (1926).
[8] M. Schulz and F. Krämer, *Farben-Ztg.,* **31,** 2556-8 (1926).
[9] H. Wolff, *Farben-Ztg.,* **31,** 2611-12 (1926).
[10] M. Marini, *Peintures, pigments, vernis,* **6,** 890-3 (1929).
[11] E. Donath, *Chem.-Ztg.,* **54,** 667 (1930).
[12] F. Michel, *Chem.-Ztg.,* **54,** 182-3 (1930).

layer which is retained for at least a day. The color changes to brown in the presence of traces of nitrites.

Leppert and Majewska[13] suggested a modification in which powdered resin or a drop of lacquer was treated on glass over a white background with a freshly prepared reagent containing 15 to 20 parts by volume of acetic anhydride and 1 part by volume of sulfuric acid (density 1.84). Rosin was reported to give a dark violet coloration which later turned blue, while Albertol gave a red coloration with no evidence of blue even on long observation. Kraus[14] studied the solubility of various resins in both hot and cold acetic anhydride as well as the color reactions obtained by adding sulfuric acid. His results are given in Table CXXXI.

TABLE CXXXI

	Solubility in Acetic Anhydride		Coloration with Concentrated Sulfuric Acid	
	Hot	Cold	Immediate	After 12 min. (diluted)
Accroides, red	e.s.*	clear	dark red	red-brown
Batjan damar	d.s.†	turbid	dark brown	olive-brown
Dewaxed damar	d.s.	turbid	dirty, light red	olive-brown
Flake shellac	e.s.	clear	yellowish	yellow
Elemi	e.s.	clear	dark, brownish red	olive-brown
Mastic	d.s.	turbid	red-brown	dirty, dark red
Rosin	e.s.	clear	dark violet-red	brown

* e.s. easily soluble. † d.s. difficultly soluble.

LaLande[15] found that the colorations produced were dependent upon the concentration of the abietic acid solution, the temperature, and the amount of sulfuric acid added. He also tabulated (Table CXXXII) the approximate time for each color change to take place. The tests were conducted by the addition of 0.05 cc. of 95 per cent sulfuric acid to 2 cc. of the abietic acid solution.

Stock[16] made a study of copal esters and fused copals and reported

[13] Z. Leppert and Z. Majewska, *Przemysl. Chem.*, **16**, 130-2 (1932); *Farben-Ztg.*, **38**, 154 (1932).

[14] A. Kraus, *Farben-Ztg.*, **38**, 322 (1932).

[15] W. A. LaLande, Jr., *J. Am. Chem. Soc.*, **55**, 1536-40 (1933).

[16] E. Stock, *Farben-Ztg.*, **39**, 141 (1934).

TABLE CXXXII

Concentration of Abietic Acid	Colorations (25°C.)
0.3 M	Blue $\xrightarrow{45^*}$ violet-blue $\xrightarrow{75}$ violet $\longrightarrow$ brown
0.2 M	Blue $\xrightarrow{17}$ greenish blue $\xrightarrow{163}$ green-black $\longrightarrow$ brown
0.1 M	Violet-blue $\xrightarrow{8}$ blue $\xrightarrow{12}$ green $\longrightarrow$ brown
0.05 M	Purple $\xrightarrow{4}$ violet $\xrightarrow{4}$ green-blue $\xrightarrow{9}$ green $\longrightarrow$ brown
0.01 M	Reddish violet $\xrightarrow{25}$ brown-violet $\xrightarrow{30}$ brown

* Time in seconds.

that genuine copals may give either positive or negative results when tested by the Storch-Morawski method.

Table CXXXIII gives the results of the Liebermann-Storch test when applied to natural resins, as reported by the London Shellac Research Bureau.[17]

A small flake of the resin is dissolved in 1 cc. of acetic anhydride. The solution is treated on a porcelain spot plate with two drops of sulfuric acid (specific gravity 1.70).

TABLE CXXXIII

Type of Resin	Liebermann-Storch Coloration
Congo	Pink
Damar	Deep red
Elemi	Orange
Kauri	Reddish brown
Manila	Pink
Natural rosin	Evanescent violet
Shellac	Weak green

The Halphen-Hicks Test. The Halphen color reaction was devised for the detection of rosin oil in mineral oil. It was modified by Foerster[18] who applied the test to the detection of rosin in admixture with other resins. Hicks[19] applied Foerster's modification to the identification of the natural varnish resins. Two reagents are involved:

Reagent A: 1 part by volume of phenol dissolved in 2 parts by volume of carbon tetrachloride.

Reagent B: 1 part by volume of bromine dissolved in 4 parts by volume of carbon tetrachloride.

[17] *Tech. Paper No. 2* (1935).

[18] P. Foerster, *Ann. Chim. Anal.*, **14**, 14 (1909).

[19] E. F. Hicks, *J. Ind. Eng. Chem.*, **3**, 86 (1911).

TABLE CXXXIV

THE HALPHEN-HICKS TEST

Resin	Colorations Observed	
	According to Hicks	According to London Shellac Research Bureau
Congo		Ill-defined brown
Damar	Brown to lilac-brown, forms rather slowly; gradually changes to distinct reddish brown (maroon).	Lilac-brown, gradually becoming redder
Elemi	Indigo-blue, forms at once, quite permanent; gradually deepens in color, sometimes becoming purplish but generally remaining a dark rich indigo.	Indigo-purple
Kauri	Azure blue, changing rapidly to purple through violet shades. Later at point farthest from bromine vapors a dark olive green forms.	Similar to rosin but much weaker
Manila	A very faint brownish green forms slowly, changes gradually to violet and finally purple. At point farthest from bromine vapors a chocolate brown usually is produced.	Similar to rosin but much weaker
Mastic	Reddish brown becoming almost carmine nearest to bromine vapors. A coffee brown tint is produced at the far side.	
Rosin	First green, then rapidly blue and violet; latter lasts considerable time then slowly changes to purple and finally a deep indigo in all parts.	Green, intense blue
Sandarac	Lilac, forms almost immediately and is quite permanent; gradually changes to a violet, becoming violet-brown farthest from bromine vapors.	
Shellac	No coloration when pure.	None
Zanzibar	A light brown, forms slowly, later brownish violet ana finally a chocolate brown mixed with some violet.	

A small amount of resin was dissolved in 1 to 2 cc. of reagent *A* and then placed in a cavity of a porcelain spot plate. A spreading effect about the rim of the cavity should be noted and a small amount of carbon tetrachloride added if the spreading fails to take place. A small amount of reagent *B* is then placed in an adjacent depression of the plate and the two depressions covered with a small watch glass so that the liberated bromine vapors come in contact with the surface of the resin solution. Hicks states that the color reactions vary from 5 to 10 minutes in duration and are best observed upon the flat portion of the plate. His results are tabulated in Table CXXXIV together with those of the London Shellac Research Bureau.[20] In the latter, the test has been modified, reagent *B* being 1 part by volume of bromine in 2 parts by volume of carbon tetrachloride. The test also specifies dissolving a flake of resin in 1 cc. of carbon tetrachloride and then adding 1 cc. of reagent *A* to it upon the spot plate.

Hicks points out that the rosin coloration is sufficiently intense to mask other colorations when present in fairly large concentrations, and also states that the presence of more than traces of water, alcohol, or ether interferes with the sensitivity of the reaction.

Individual Reaction Tests. The London Shellac Research Bureau[21] has reported a color reaction for the identification of resins in which a small amount of resin is dissolved in 2 cc. of benzoyl chloride and the solution cooled. Two tests are made, the first (*A*) by adding one drop of the benzoyl chloride solution to 2 cc. of concentrated sulfuric acid and the second (*B*) by adding one drop of concentrated sulfuric acid to the remainder of the benzoyl chloride solution. Colors developed are given in Table CXXXV.

The authors, on application of this test, have found that certain soft Manila copals give results similar to that described for rosin.

Brauer[22] studied the color reactions of the resins in an attempt to find "group reactions" by means of which the presence of resin in linseed oil might be detected, as well as "individual reactions" by which the resins might be differentiated. As the group reaction, he proposed the use of phosphomolybdic acid and ammonia, which with most resins yields a deep blue coloration. The tests were in ether solution in which linseed oil gives only a pale green coloration. To differentiate between the individual resins, Brauer proposed two reactions, the first using a solution of ammonium molybdate in concen-

[20] *Tech. Paper No. 2* (1935).

[21] *Tech. Paper No. 2* (1935).

[22] K. Brauer, *Chem.-Ztg.*, **50**, 371-2 (1926).

TABLE CXXXV

Resin	Benzoyl Chloride Test	
	First test (*A*)	Second test (*B*)
Rosin	Deep orange	Red changing to purple
Congo	Orange-red	Orange-brown
Kauri	Brown	Brown
Manila	Brown	Brown
Damar	Reddish brown	Orange-brown
Shellac	Orange-brown	Yellowish brown
Elemi	Brown	Brown

trated sulfuric acid, and the second a potassium hydroxide solution of diazotized sulfanilic acid. He also recorded the colorations obtained with concentrated sulfuric acid alone. Brauer's results are given in Tables CXXXVI, CXXXVII, CXXXVIII, and CXXXIX. The sul-

TABLE CXXXVI

Resin	Diazotized Sulfanilic Acid (coupled) in KOH Solution
Amber	Dark orange-red (dissolved in chloroform)
Damar	Light orange-red
Dragon's blood	Blood red
Rosin	Dark red-orange
Borneo copal	Red-brown
Manila	Red-orange
Zanzibar copal	Dark brown-red
Mastic	Light red-orange
Shellac	Purple-red

furic acid-ammonium molybdate reagent was prepared by adding 0.1-0.2 g. of finely powdered ammonium molybdate to 5 cc. of concentrated sulfuric acid and shaking vigorously.

Fonrobert and Pistor[23] modified the procedure slightly, using an ether-alcohol solvent in which the resins were more readily soluble, and extended it to include a variety of synthetic resins, phenol, tetrahydroxyabietic acid, indene, turpentine, and linseed oil with and without small percentages of rosin. The results were only partially in agreement with Brauer. The method was stated to be unsatisfactory for the

[23] E. Fonrobert and K. Pistor, *Chem.-Ztg.*, **51**, 139-40 (1927).

TABLE CXXXVII

Resin	Coloration with Phosphomolybdic Acid		
	Alone	+ Ammonia	+ Sulfuric acid
Abietic acid, pure	Light yellow	No (or scarcely noticeable) reaction	Colorless
Accroides	Yellow-red	Discolored brown-green	Dirty blue-green
Congo	Yellow-green	Scarcely visible bluish	Almost colorless
Congo, fused	Yellow-green	Light blue	Weak bluish
Rosin, American (wood)	Yellow	Dark blue	Gray-blue
Rosin, German	Yellow	Light blue	Blue-green
Rosin, Spanish	Yellow	Blue	Intense heightening of color

detection of rosin in the presence of other resins, whether natural or synthetic, and subject to color variances induced by the manipulative differences in the method as employed by different investigators. The

TABLE CXXXVIII

Resin	Coloration with Phosphomolybdic Acid					
	Alone		+ Ammonia		+ Sulfuric acid	
	According to Brauer	Observed	According to Brauer	Observed	According to Brauer	Observed
Amber (dissolved in chloroform)	Green	Yellow	Deep blue	Light blue	Deep blue	Almost colorless
Damar	Yellow	Yellow	Pale blue	Pale blue	Pale blue	Very pale
Dragon's blood	Olive green	...	Olive green	...	Blue-green	...
Rosin	Green	Yellow	Deep blue	Deep blue	Prussian blue	Somewhat brighter
Borneo copal	Yellow	Sky blue	...	Marine blue	...	...
Manila	Yellow	Yellow	Prussian blue	Pale blue	Light green	Almost colorless
Zanzibar copal	Yellow	...	Pale blue	...	...	...
Mastic	Yellow	...	Light blue	...	...	...
Shellac	Yellow	Yellow-brown	Pale blue	Dirty gray to brown-lilac	Pale blue	Greenish

results of Fonrobert and Pistor are given in Tables CXXXVIII and CXXXIX. The ammonia was a 10 per cent solution.

TABLE CXXXIX

Resin	Coloration with Sulfuric Acid and Ammonium Molybdate					
	Alone		After 15 minutes		+Ammonia	
	According to Brauer	Observed	According to Brauer	Observed	According to Brauer	Observed
Amber	Light green	Nearer green-blue	Unchanged	Unchanged	Colorless	Colorless
Damar	Dark blue	Nearer green-blue	Unchanged	Unchanged	Greenish-yellow (upper layer)	Weak yellowish, upper layer brown
Dragon's blood	Dark (Russian) green	...	Unchanged	...	Red	...
Rosin, Spanish	Prussian blue	Dark blue	Unchanged	Deep green	Stiffens to a yellowish gelatinous mass	Orange; resin separates
Borneo copal	Blue-green	...	Unchanged	...	Colorless	...
Manila copal	Green-blue	Blue	Unchanged	...	Weak yellow	Yellow
Zanzibar copal	Green-gray	...	Unchanged	...	Colorless	...
Mastic	Navy blue	...	Unchanged	...	Yellow (lower layer)	...
Shellac	Light green (jade green)	Dark green	Unchanged	Unchanged	Lilac	Blue-red to red-yellow
Abietic acid, pure	...	Dark blue	...	Dark blue	...	Color disappears

Donath[24] described a method for the detection of rosin in which one gram of powdered resin is boiled in 5 cc. of nitric acid (specific gravity 1.32-1.33) for a period of one minute. The mixture is cooled and diluted with an equal volume of distilled water. Upon addition of an excess of ammonia, colors develop which are progressively intensified in all cases except those of Albertol resins. Rosin was reported to give an orange coloration deepening in one day to a deep brown-red. Donath discusses the application to mixtures of rosin with waxes, tallow, etc., and in the presence of cholesterol. Stock[25] studied the Donath reaction, applying it to natural resins. He recorded the immediate coloration and the color on standing 5 minutes, one hour, and one day. The results are given in Table CXL.

[24] E. Donath, *Chem.-Ztg.*, **54**, 667 (1930).
[25] E. Stock, *Farben-Ztg.*, **36**, 1176-7 (1931).

TABLE CXL

The Donath Test

Resin	Color Reaction			
	Immediate	After 5 minutes	After 1 hour	After 1 day
Damar	Light wine yellow	Yellow-reddish	Yellow-red	Yellow-brown
Kauri				
Bush kauri	Light reddish mahogany	Red-brown	Light brown-red	Light brown-red
Brown kauri	Light yellow	Yellow-red	Dark red-brown	Dark red-brown
Copals				
Manila	Light ruby red	Red-orange	Wine red	Wine red
Pontianak	Light yellowish red	Wine red	Wine red	Wine red
East African copals				
Madagascar	Light yellow-red	Light wine red	Wine red	Wine red
Zanzibar goose-skin	Light yellow-red	Wine red	Blood red	Blood red
West African copals				
Accra	Light red-yellow	Light wine red	Light red	Light red
Angola	Light reddish yellow	Yellow-red	Wine red	Wine red
Benguela	Reddish yellow	Wine red	Wine red	Wine red
Congo	Yellow-red	Blood red	Blood red	Blood red
Sierra Leone	Light yellow-red	Wine red	Wine red	Wine red
South American copals				
Brazil, fossil	Light yellow-red	Red-yellow	Red-yellow	Red-yellow
Demerara (Colombia)	Entirely light brown	Wine red	Wine red	Wine red
Miscellaneous resins				
Accroides	Blood red	Dark red	Deep dark red	Deep dark red
Amber, fused	Very weak cloudiness	Weak yellowish cloudiness	Greenish cloudiness	Greenish cloudiness
Amber	Light yellow	Somewhat yellow	Wine yellow	Wine yellow
Dragon's blood	Yellow-red	Wine red	Dark wine red	Dark wine red
Ester gum	Orange	Red-orange	Dark red-orange	Red-brown (wine red)
Gamboge	Light brown	Dark red	Deep dark red	Deep dark red
Elemi	Light yellowish red	Yellow-red	Wine red	Wine red
Mastic	Light red then reddish yellow	Reddish brown	Dirty light red	Dirty light red
Rosin	Orange	Red-orange	Dark red-orange	Red-brown (wine red)
Sandarac	Light yellow-reddish	Blood red	Blood red	Blood red
Shellac	Greenish yellow, clear	Reddish yellow, turbid	Wine yellow, turbid	Wine yellow, turbid
Varnishes and siccatives				
Cobalt oleate	Red-yellow	Dark wine red	Dark wine red	Dark wine red
Cobalt resinate	Light brown	Dark wine red, turbid	Dark wine red, turbid	Dark wine red, turbid
Copal varnish	Light yellow	Light yellow	Light yellow	Reddish yellow
Lead-manganese oleate	Light yellow	Yellow-red	Yellow-red	Yellow-red
Lead-manganese-resinate	Red-yellow	Dark wine red, turbid	Dark wine red, turbid	Dark wine red, turbid
Manganese resinate	Light brown	Dark wine red, turbid	Dark wine red, turbid	Dark wine red, turbid

Hirschson's Color Reactions. Coffignier[26] described the color reactions developed by Hirschson using Haller[27] as his reference. Hirschson's tests combine solubility with color reactions and precipitation effects as a means of resin identification. Three reagents are described:

(A) Bromine 1 to 20 in chloroform.
(B) Iron perchloride 1 to 10 in 95 per cent alcohol.
(C) Iodine in petroleum ether (boiling range 35 to 40°C.)

Tests for the various resins are given in Table CXLI.

TABLE CXLI

Accroides, red	Completely soluble in alcohol, red, colored dark brown by reagent B. Not precipitated by lead acetate. The chloroform extract is colorless.
Accroides, yellow	Same as red accroides but the alcoholic solution is yellow.
Coniferous resins and balsams	Alcoholic solution is colored brown or greenish with reagent B. Product is largely soluble in sodium carbonate solution; it is colored red-violet with bluish stripes.
Damar	The etherized solution is disturbed by alcohol and hydrochloric alcohol produces a brown tint. The petroleum ether insoluble material is colored green by chloral hydrate.
Elemi	Completely soluble in alcohol but not soluble in sodium carbonate solution. Solution in reagent A gives a green coloration which upon addition of hydrochloric acid assumes a violet or blue tint.
Gum-lac	The alcoholic solution is not disturbed by ammonia but is colored violet. Subsequent addition of lead acetate precipitates the mixture in a violet tint.
Manila	Incompletely soluble in alcohol. The chloroform solution does not give a precipitate when treated with reagent A.
Mastic	Partly soluble in petroleum ether. Red-violet coloration with reagent C.
Sandarac	Precipitated from alcoholic solution by lead acetate. Precipitate remains when heated.

The Chlorosulfonic Acid Test. Cohen[28] describes a test in which chlorosulfonic acid in chloroform in the proportions of 1 to 5 by volume is added to a chloroform solution of the resin. Rosin is stated to give a violet-red coloration, whereas ester gum and Albertols produce a rose-red color. Cohen states that linseed oil, tung oil, stand oils, and oleic acid give no reaction. Investigation of various copals and var-

[26] C. Coffignier, "Varnishes: Their Chemistry and Manufacture," pp. 160-1, Scott, Greenwood & Son (1923).
[27] Haller, "Memento du chimiste," pp. 601-4.
[28] H. C. Cohen, *Farben-Ztg.*, **36**, 121 (1930).

nishes showed that only varnishes containing run resins give a positive reaction.

The Phloroglucinol Test. Reinitzer[29] reported that many resins give a cherry-red coloration when tested with phloroglucinol. A few crystals of phloroglucinol are placed on a freshly fractured surface of the resin and a few drops of alcohol added. When the alcohol has nearly evaporated, the surface is treated with a drop of concentrated hydrochloric acid. Among the many materials stated to give this test are red and yellow accroides, manila, elemi, mastic, and the alcohol-soluble portion of damar.

Identification of Resins by Means of Chemical and Physical Properties. Among the more common properties usually investigated are acid value, saponification value, iodine number, refractive index, solubility in various solvents, color and viscosity of the resulting solutions, softening point and melting point. The method is satisfactory when pure resin samples are to be investigated, but frequently presents difficulties when applied to commercial products or samples in which more than one resin is present. The methods employed are discussed in detail in Chapter XXVI.

Coffignier[30] describes a comprehensive system of identification utilizing solubilities, precipitation effects, and color reactions which he attributes to Gillet.

Identification by Determination of Resin Constituents. The compositions of the majority of natural resins have been determined, the work being largely that of Tschirch and his colleagues. The methods are far too specialized and time-consuming to permit their use as a means of resin identification in commercial laboratories.

Fluorescence Analysis. Wolff and Toeldte[31] investigated the fluorescence of varnish resins under ultraviolet light as a means of identification. The resins were examined in the form of lumps, powder, butyl acetate solution, and residue from evaporation of the butyl acetate solution. Examination in the form of lumps proved to be unsatisfactory. Indications could be obtained from the other three forms. Results are given in Table CXLII.

Increased intensity was noticed when the resin acidity was neutralized. It was stated that combination of microscopic, capillary, and fluorescence analysis would permit differentiation between resins previ-

[29] F. Reinitzer, *Z. anal. Chem.*, **69**, 114-21 (1926).

[30] C. Coffignier, "Varnishes: Their Chemistry and Manufacture," p. 160, Scott, Greenwood & Son, London, 1923.

[31] H. Wolff and W. Toeldte, *Farben-Ztg.*, **31**, 2503-5 (1926).

TABLE CXLII

FLUORESCENCE OF RESINS

Resin	Powder	Butyl Acetate Solution	Residue from Evaporation of Butyl Acetate Solution	According to London Shellac Bureau
Amber, fused	Light green	Light blue	Light bluish green	...
Congo	Light blue	Light blue	Blue	Blue
Damar	Gray-blue	Gray-blue	Blue	Weak blue
Dragon's Blood	...	Reddish yellow	...	...
Elemi	...	...	...	Orange
Kauri	Green	Blue	Blue	Weak bluish green
Manila	Greenish blue	Greenish gray	Bluish gray	Weak blue
Mastic	Bluish gray	Blue	Light blue	...
Rosin	Gray-green	Green	Bluish green	Weak blue
Rosin, hardened	Light blue	Light blue	Light blue	...
Sandarac	Bluish green	Greenish gray	Bluish gray	...
Shellac	Orange-red	Orange-red	Orange-red	Orange-red

ously unclassifiable. Oil varnishes[32] gave less distinct results than obtained with the original resins. The siccative and method of drying were found to have a profound influence on the fluorescence of the resin. Stock[33] used the quartz lamp as a means of detecting the adulteration of sandarac with rosin and pistachio resin. The fluorescence of the resins as reported by the London Shellac Research Bureau[34] will be found in Table CXLII.

Capillary Analysis. Stock[35] studied capillary analysis. Dried strips of filter paper after partial immersion in resin solutions for periods up to twenty-four hours were examined for color, extent, opacity, and intensity. The tests must be conducted under controlled conditions. Stock found that he could obtain information as to the identity and purity of the resins by examination of the zones formed on the filter paper. Wolff and Toeldte[36] studied the combined use of capillary and fluorescence analysis and found the results to be more satisfactory

[32] H. Wolff and W. Toeldte, *Farben-Ztg.*, 32, 80-1 (1926).
[33] E. Stock, *Farben-Ztg.*, 35, 1459-60 (1930).
[34] *Tech. Paper No. 2* (1935).
[35] E. Stock, *Farben-Ztg.*, 31, 1903-4, 1959-60, 2133-4, 2187-8, 2240-3 (1926).
[36] H. Wolff and W. Toeldte, *Farben-Ztg.*, 32, 294-6 (1926).

for the identification of resins than fluorescence analysis alone, the zones of fluorescence often being more distinct. Fonrobert and Pistor[37] investigated Stock's capillary analysis and found it satisfactory for the examination of new and pure resin samples but not adapted to the accurate analysis of mixed samples.

Microscopic Identification. Stock[38] found the microscopic examination of relatively thick specimens to be satisfactory and tabulated the source, chemical constants, macroscopical and microscopical characteristics, together with photomicrographs for a variety of varnish copals.

Unfortunately none of the existing methods for the detection and identification of natural resins is infallible. Many of the investigations cited have included synthetic resins which give results strikingly similar if not exactly similar to those of natural resins. The color reactions of such materials have not been discussed here but must be considered in the application of the tests described. Thus, a positive test by any one method does not necessarily constitute a conclusive result but is merely an indication to be confirmed by further tests.

A concise description of a color or color variation sufficiently accurate to permit identification by others is difficult. Color variations are infinite, depending upon the color sensitivity of the eyes of the individual. The recorded color observations permit the elimination of those resins which give colors far removed from that of the unknown material. The decision as to the coloration involved must be made by a comparison of the coloration of the unknown material with those of the known resins giving similar shades.

An important factor is the concentration of the materials present during the examination of the coloration.

The controversial nature of the literature has done much to discredit the value of some methods, particularly in those cases in which individual technical publications have been considered rather than the entire available literature. The utility of these methods is perhaps best stated in the words of Brauer:[39]

> While one must guard against over-estimating color reactions, it does not, however, appear proper to disregard or underestimate them. Probably a painstaking analyst would not depend upon the color reactions alone. They do, however, give him immediately a most important indication as to

[37] E. Fonrobert and K. Pistor, *Farben-Ztg.*, 32, 2424-9 (1927).

[38] E. Stock, *Farben-Ztg.*, 30, 2340-1, 2407-9, 2475-7, 2542-5, 2604-6, 2668-70 (1925).

[39] K. Brauer, *Chem.-Ztg.*, 50, 371-2 (1926).

which resins are present and widen the investigation so that a logical conclusion can be reached.

The authors have found that, with application of the necessary precautions with reference to duplication of procedure and comparison with known samples, little difficulty is incurred in the identification of pure samples of individual resins. The results of one test should not, however, be taken as conclusive but should be confirmed by other methods. The examination of resin mixtures particularly demands the utilization of every available method as a check upon the results obtained. For mixed samples, none of the methods available are completely satisfactory and much depends upon the ability of the analyst to apply judiciously such indications as may be obtained from the various tests.

For the sake of completeness, a few references[40] have been included for the detection and identification of synthetic resins.

[40] T. F. Bradley, "Methods for the Detection and Identification of Synthetic Resins," *Ind. Eng. Chem., Anal. Ed.,* **3**, 304-9 (1931).

E. A. Stoppel, "The Identification of Synthetic Resins in Finished Products," *Off. Dig. Fed. Paint Varnish Prod. Clubs, No. 126,* 189-92 (1933).

J. H. Frydlender, "Methods for the Detection and Identification of Synthetic Resins," *Rev. prod. chim.,* **35**, 129-35 (1932).

H. Wagner and Herm. Schirmer, "The Chemical Identification of Artificial Resins Used in Lacquers and Varnishes," *Farben-Ztg.,* **43**, 131-3, 157-8 (1938).

CHAPTER XXVI

PHYSICAL AND CHEMICAL TESTING METHODS

The testings of natural resins may be carried out either for the control of quality or as a routine investigation of their properties in the assembling of basic information. In the first case, usually only dirt and color determinations are made. Chemical properties and most of the other physical properties are fairly constant within each grade and are of small use as an indication of quality, save for the detection of any irregularity an adulterant might cause. Adulteration is rare in today's natural resin market because of the rigid control exerted by the governments of producing countries.

In the determination of per cent insoluble content, insoluble deposition, viscosity, and color, the solvent used is either toluol or alcohol, the choice being made from the following list:

Toluol	Ethyl Alcohol (U.S.P. 95 per cent)
Batavia damar	Macassar manila
Singapore damar	Philippine manila
Batu	Singapore manila
Black east india	Pontianak
Pale east india	Boea
Elemi	Mastic
	Sandarac
	Accroides

Insoluble Content. The most important determinations from the standpoint of quality are those of insoluble content. Two methods are in general use: (1) the insoluble deposition test, in which the volume of insoluble matter is measured; (2) the per cent insoluble content test, in which the weight of insoluble matter is determined as a percentage of the original sample.

The first test is the more popular because of its simplicity, but suffers the disadvantage that unless the sample is well ground, the result is a function of the particle size as well as the true volume of insoluble matter. Another drawback is that, owing to the difference in density between siliceous and woody impurities, it is possible for one sample containing a greater percentage of insoluble matter, chiefly

of a siliceous nature, to give lower insoluble deposition volumes than a second sample, actually containing less insoluble matter, but this of a woody nature.

Determination of Insoluble Deposition. This test is carried out in a specially designed tube, shown in Fig. 78. The tube is filled with solvent to the 40-cc. mark and 10 g. of a representative sample of well-powdered resin added.

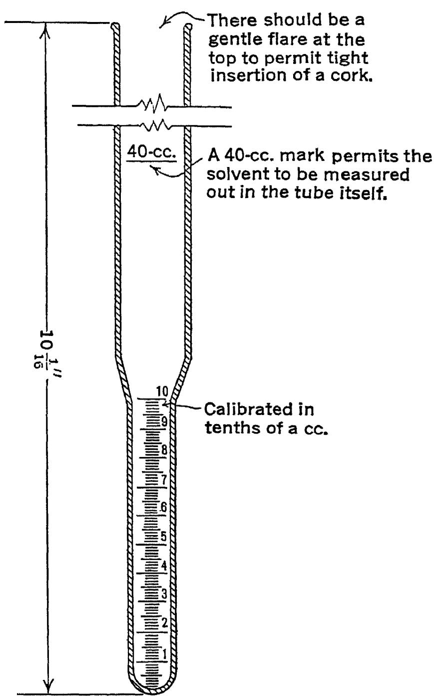


FIG. 78. Insoluble deposition tube.

The resin should be weighed on a balance correct to 0.1 g. After solution has taken place, the tube is allowed to stand in an upright position for 24 hours to permit the insoluble matter to settle. If, upon inspection at any intermediate time, the level of the sediment appears uneven enough to prohibit an accurate reading of the volume of deposition, proper leveling can be secured by judiciously tapping the side of the tube. If recourse to such tapping is necessary, another 24 hours must elapse before taking the reading. The volume of deposition is read off in cubic centimeters or tenths thereof. The test is run in duplicate and the result taken as the average of the two determinations.

The procedure gives a rapid evaluation of a sample.

Even settling can be obtained by rapidly rotating the tube by hand imme-

diately prior to placing it in its vertical settling position. Its contents are then in a swirling motion and even deposition is likely. The time to effect solution will depend upon the facilities available. Solution should be complete before beginning the settling period.

Determination of per Cent Insoluble Content. Five grams of a representative sample of powdered resin is dissolved in 10 to 20 cc. of solvent by gentle heating. The hot solution is decanted through a weighed Jena glass filter crucible by applying suction as shown in Fig. 79. (This crucible, No. 1G1, is

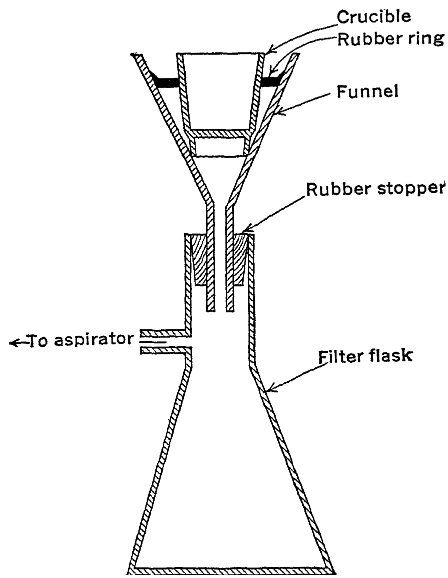


FIG. 79. Filtering setup for per cent insoluble determination.

made of Jena or chemically resistant glass and has a fritted glass bottom for filtering. It is a tall form used especially for filtering out gelatinous matter.) The residue is retained in the beaker and washed several times with hot solvent. The wash solvent is also decanted through the crucible. The residue is finally transferred to the crucible by rinsing with hot solvent.

After filtering, the crucible is placed in the extraction flask and extracted with 50 to 60 cc. of solvent for two hours. It is then dried in an electric oven at 105°C. for 1 hour, cooled in a desiccator, and weighed. The gain in weight of the crucible represents the insoluble matter present in the original sample. All weighings in this determination should be done on an analytical balance and results reported to three significant figures. Before placing the crucible in the oven, care should be taken that no resin film remains on the inner wall

of the crucible. If such a resin deposit be present, it can be removed by wiping with a solvent-moistened cloth.

In connection with the extraction operations, it was found necessary to design a suitable extraction flask, Fig. 80. Within it, the crucible is held in place by means of two rows of indentations in the flask wall. The indentations on the lower level are the means of support, while those of the upper level act merely to prevent tipping. There are three indentations spaced 120 degrees apart at each of the two levels. No wires or other cumbersome means of support are needed. The neck of the flask is short enough to permit the insertion or withdrawal of the crucible by ordinary laboratory forceps.

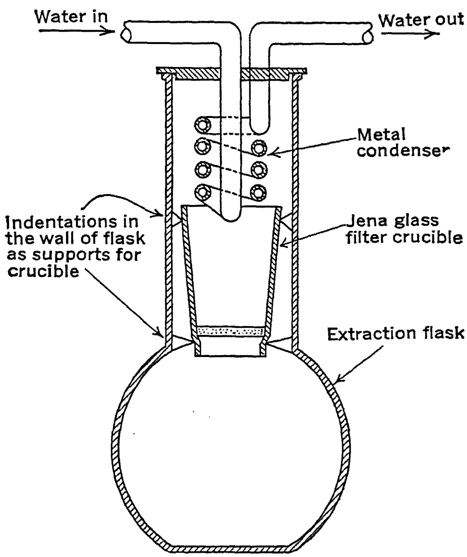


FIG. 80. Extraction apparatus used in per cent insoluble content test.

It is important that the crucible be cleaned after each use. Failure to do so will lengthen the filtering time considerably, if not entirely stop the flow. Cleaning is best done by soaking the crucibles in sulfuric acid for several hours, or overnight if possible. Washing the crucible free of acid restores it for further use.

Ash Content. The ash content of a resin indicates the amount of mineral matter present and is of little importance save to determine the ratio of mineral to vegetable impurities. For any of the better grades of resin, ash content is negligible. It is only in the "dust" grades that mineral matter approaches or exceeds parity with vegetable impurities.

Determination of Ash Content. A 2-g. sample of crushed resin is placed in

a weighed crucible and ignited. After the flames have subsided, the residue is ashed to constant weight, cooled, and weighed. The residue represents the ash content and is reported as a percentage of the original sample.

Color. Perhaps on a par in importance with the dirt determination is that of color. This is performed on a 50 per cent solution of the resin.

Determination of Color. A nominal 50 per cent solution is prepared by mixing equal weights of resin and solvent. The resin is cold-cut in a closed jar and insoluble matter allowed to settle. The color is obtained by placing the solution in a viscosity tube (see next test) and matching against the Gardner Color Scale.

The Gardner Color Scale, a set of color standards widely used in the paint industry, consists of eighteen tubes ranging from a water-white (No. 1) to a dark brown (No. 18). Each tube contains a sealed solution two-thirds darker than the preceding color.

As originally designed, the color standards were prepared from potassium dichromate-sulfuric acid solutions of varying concentrations. The darkest tube (No. 18) contained exactly 3 g. of potassium dichromate ($K_2Cr_2O_7$) per 100 cc. of sulfuric acid. These solutions have since been replaced by combinations of ferric chloride, cobaltous chloride, and hydrochloric acid. In their preparation, a solution of ferric chloride in 2 per cent hydrochloric acid, equal in color to that of 3 g. of potassium dichromate in 100 cc. of sulfuric acid, is first made. This solution is designated as No. 18 and all others are derived from it. Thus, the No. 18 solution is diluted until a 15-mm. layer of it in a Duboscq colorimeter is equal in intensity to a 10-mm. layer of the undiluted solution. Because dilution produces too green a color in the middle and lower ranges, it is necessary to add various amounts of cobaltous chloride. The ferric chloride solution contains about 5 parts $FeCl_3.6H_2O$ and 1.2 parts 2 per cent hydrochloric acid in water. The cobaltous chloride solution contains 1 part $CoCl_2.6H_2O$ and 3 parts of 2 per cent hydrochloric acid in water. These solutions are the stock liquids from which the eighteen standards are prepared. The amounts of each, along with 2 per cent hydrochloric acid, are given below:

No.	1	2	3	4	5	6	7	8	9
Fe Liquid	0.13	0.19	0.29	0.43	0.65	1.00	1.7	2.5	3.3
Co Liquid	0.19	0.29	0.43	0.65	0.97	1.3	1.7	2.0	2.6
2% HCl	99.68	99.52	99.28	98.92	98.35	97.7	96.6	95.5	94.1

No.	10	11	12	13	14	15	16	17	18
Fe Liquid	5.1	7.5	10.8	16.6	22.2	29.4	37.8	51.3	100.0
Co Liquid	3.6	5.3	7.6	10.0	13.3	17.6	22.8	25.6	0
2% HCl	91.3	87.2	81.6	73.4	64.5	53.0	39.3	23.1	0

Viscosity. The tube containing the resin solution can also be used in the determination of viscosity.

Determination of Viscosity. A nominal 50 per cent solution is prepared by mixing equal weights of resin and solvent. The resin is cold-cut in a closed jar and insoluble matter allowed to settle. If a solution is already on hand from the color determination this can be used. The solution, in a viscosity tube, is matched against the Gardner-Holdt Bubble Viscosimeter. The bubble viscosimeter consists of a series of sealed tubes filled with mineral oils of definite viscosities. The tubes containing the standard oils are 10.65 mm. in diameter and approximately 11 cm. long. The solution of unknown density is poured into a tube of the same diameter and length and the tube corked, leaving an air space the same size as that in the standard tubes. Unknown and standards are brought to 25°C., held in an upright position, and inverted. The viscosity of the sample is reported as that of the standard having a bubble which moves at the same rate as the bubble in the sample tube.

Bubble viscosities may be converted to absolute viscosities according to Table CXLIII.

TABLE CXLIII

ABSOLUTE VISCOSITIES (POISES) AT 25°C. CORRESPONDING TO BUBBLE VISCOSITIES

A	0.50	L	3.00	W	10.70
B	0.65	M	3.20	X	12.9
C	0.85	N	3.40	Y	17.6
D	1.00	O	3.70	Z	22.7
E	1.25	P	4.00	Z1	27.0
F	1.40	Q	4.35	Z2	36.2
G	1.65	R	4.70	Z3	46.3
H	2.00	S	5.00	Z4	63.4
I	2.25	T	5.50	Z5	98.5
J	2.50	U	6.27	Z6	148
K	2.75	V	8.84		

Solubility. Any method for determining the solubility of resins must be of an arbitrary nature due to the factors of time and temperature. The procedures favored by previous investigators, involving extraction, boiling, or long periods of contact between resin and solvent, yielded results of dubious value to the resin consumer. Moreover, the

concentration of the resin in the attempted mixture was usually much lower than that prevailing in commercial preparations.

A more desirable solubility determination would be one in which the resin is dissolved in a logical volume of solvent without the use of heat. It is this latter type that the authors have developed. The results from such a method are of greater value than those from the former types, inasmuch as the concentration used and the mode of preparation more effectively approximate commercial practice. Determination of solubility is discussed on p. 101, Chapter XIII.

Fusion Points. Resins, lacking a crystalline structure, do not possess a sharp melting point, but rather undergo a gradual fusion when heated. On heating, two critical temperatures may be observed: the first, known as the softening point, is evidenced by softening and blunting of the sharp edges of the resin; the second, termed the melting point, is evidenced by actual liquefaction. The melting point as used here does not have quite the same significance as it does for crystalline substances or even such amorphous materials as tar, pitch, or glue. In these, no decomposition occurs, whereas with resins part of the essential oil is driven off and minor physical and chemical changes occur. Moreover, the critical points are usually designated by a short range of temperature rather than by a sharp point. In general, the two are separated by about 30 to 40°C., except in certain Congo copals where as much as a 100-degree difference may exist.

Determination of Softening Point. A sample of ground resin is placed in a capillary melting-point tube and heated in a liquid bath. The temperature at which the sharp edges of the resin particles appear to become round is taken as the softening point. This is a rather indefinite value and difficult for two operators to agree upon.

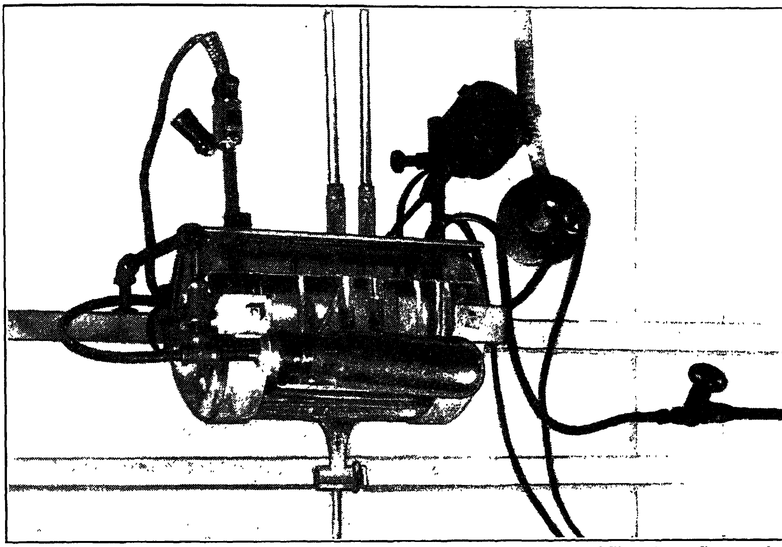
Determination of Melting Point. An 0.2-g. sample is gently sintered to the bottom of a wide-form porcelain crucible of about 17-cc. capacity. One hundred grams of mercury, previously heated to about 30°C. below the probable melting point of the resin, is poured in over the cooled sample and a thermometer bulb immersed. The crucible is heated slowly (2 to 4 degrees per minute). The temperature at which the first bit of resin appears at the surface of the mercury is reported as the melting point. This method is a further modification of Rangaswami's[1] modification of the Durrans[2] method. The former prescribed only 25 g. of mercury, but the larger amount has been found to give the same values and to be easier to handle.

A modification of the mercury method has been developed and

[1] M. Rangaswami, *J. Oil Colour Chem. Assoc.*, **13**, 287 (930).
[2] T. H. Durrans, *J. Oil Colour Chem. Assoc.*, **12**, 173 (1929).

adopted by the Stroock and Wittenberg Corporation, which permits rapid determinations of more consistent accuracy. The apparatus (Fig. 81) consists essentially of an electrically heated glass bath provided with a stirring device to ensure a uniform temperature. Six determinations are run at once. The exact procedure follows:

1. Three grams of freshly powdered resin are placed in a test tube which is gently heated until the mass is molten. The tube is then set aside until the resin has solidified.



Courtesy Stroock and Wittenberg Corporation

FIG. 81. Improved apparatus for determining melting points by the mercury method.

2. Fifty grams of mercury are added on top of the cold resin. A thermometer, held in place by a split cork, is then inserted in the mercury layer.
3. The tube is placed in the bath which has been heated to within 20 to 30°C. of the approximate melting point of the resin. If several resins are run at the same time, the bath should be heated to within 20 to 30°C. of the one with the lowest melting point. However, if these melting points vary greatly (approximately 50°C.), it is preferable to divide the resins into ranges of low, medium, and high melting points, and to run each group separately.
4. The bath, while being constantly stirred, is then heated at the rate of 3°C. per minute.
5. The melting point is taken as the temperature indicated by the thermometer when the resin layer breaks through the surface of the mercury.

For adding the mercury, a 500-cc. bottle with two top inlets and one outlet

on the side near the bottom is used. A glass funnel with filter paper is inserted in one of the top openings; the other serves as a vent. Spent mercury is reclaimed by punching a pinhole through the paper to allow the mercury to pass while the resin particles are held back. A small pipet of about 5-cc. capacity is used for transferring the mercury to the test tube. The pipet is filled with mercury to a mark indicating the 50-g. level by opening a stopcock attached to the bottom outlet of the bottle.

Petrolatum or white oil has been found preferable to glycerin as the heating medium in the bath.

The preceding methods suffer the drawback that the sample when sintered to the bottom of the crucible or melted in the tube is actually run to a certain degree. The result obtained, therefore, is not the true melting point of the original resin. Although the difference is not particularly important, a method has been proposed to eliminate it. The alternate procedure involves heating a piece of resin in a similar manner, but with the resin enclosed within a small wire basket instead of being sintered to the bottom of the crucible. In this manner, pre-melting of the sample is avoided.

Specific Gravity. The specific gravities of natural resins are all within a narrow range, 1.04 to 1.08. This property, therefore, is of little or no value as a means of distinguishing one variety from another. It is of value, however, in distinguishing between natural and synthetic resin, for synthetics are uniformly of greater density. Bradley[3] has generalized on this as follows:

> If the density of a resin is above 1.15, the resin is of synthetic origin but may contain rosin, oils, or fatty acid modifying agents. If the density lies between the limits 1.10 to 1.15, the resin may comprise a cumarone-indene polymer, shellac, or a synthetic resin of the modified type. If less than 1.10, the resin is probably of natural origin but may be a soft grade of cumarone-indene resin or some other type of synthetic resin modified by considerable rosin and oils or fatty acids.

The lower density of natural resins is a point in their favor, for it indicates a higher bulking value.

Determination of Specific Gravity. A series of salt solutions of specific gravity 1.020, 1.030, 1.040, etc., as checked with a Westphal balance, is made up. A piece of the resin sample is thoroughly wet with water, then dropped into each solution. The specific gravity of the resin is reported as that of the least dense salt solution in which it will float.

Refractive Index. Like specific gravity, the refractive index is of doubtful value as a means of distinguishing between different varieties of natural resins. It is of some slight value as a method for determining

[3] T. F. Bradley, *Ind. Eng. Chem., Anal. Ed.,* 3, 304 (1931).

their synthetic or natural origin, as the latter possess somewhat lower values.

Determination of Refractive Index. The refractive index is obtained indirectly. A series of resin solutions is prepared (all in the same solvent but of different concentrations) and the indices measured by means of a refractometer. With these values of refractive index plotted against resin concentration, the index for the pure resin is obtained by extrapolation to the ordinate representing 100 per cent resin concentration.

Moisture Content. Moisture determination results will always include a certain amount of volatile oil along with the true water content. Two general methods are available: (1) heating above the boiling point of water; (2) heating below the boiling point of water to minimize the loss of oil.

Determination of Moisture Content. *First Method.* Two to 3 g. of the finely ground sample is spread out in a Petri dish or an inverted can lid about 5 cm. in diameter and left 3 hours in an oven at 105°C. The sample is cooled in a dessicator and weighed. The loss in weight is assumed to be moisture.

Second Method. The procedure calls for 5 g. of a powdered sample in a flat-bottomed dish about 4 in. in diameter. The dish is placed in a well-ventilated electric oven for at least 6 hours at 60°C. ± 2°C. The sample is cooled in a desiccator and weighed. Heating is continued to constant weight and the weight loss calculated as percentage moisture.

Damar Resene Content. Determination of the amount of β-resene (damar wax) present in damar resins usually follows one of two methods. In the first, any dirt in the original resin is reported along with the wax as per cent "wax." The test, although crude, is of value as an indication of the total loss to be expected from a dewaxing treatment. In the second method, extraneous matter is separated from the wax and the result reported as per cent β-resene. A scale accurate to one-tenth of a gram is satisfactory for the first method, whereas the small quantity handled in the second demands an analytical balance.

Determination of per Cent "Wax." Fifty grams of the sample is dissolved in 50 g. of toluol. Fifty grams of ethyl alcohol is then added with stirring and the mixture covered and allowed to stand 24 to 48 hours. The liquid is decanted off, the lower part being filtered if feasible. The solid (wax) is dried overnight at 110 to 120°C. and then weighed, its weight being calculated to per cent "wax" which includes per cent of insoluble content of the particular grade of resin.

Determination of per Cent β-Resene. Two grams of the sample is dissolved in 10 cc. of a 10 to 1 toluol-alcohol mixture and filtered to remove impurities. For this purpose an unweighed Gooch crucible or Jena glass filter

crucible can be used. To the filtrate is added 100 cc. of ethyl alcohol and the mixture allowed to stand overnight. The wax precipitate is then filtered through a weighed crucible, washed with a little 3 to 1 alcohol-toluol mixture, dried in an electric oven at 105°C. for one hour, cooled, and weighed. The residue within the crucible is calculated as per cent β-resene.

Acidity. Two general procedures are used: (1) direct titration of the resin solution with alcoholic potassium hydroxide; (2) indirect titration, in which the resin solution is allowed to stand in contact with an excess of potassium hydroxide for a definite period and then back-titrated with acid. The former method has found the greater favor.

Determination of Direct Acid Number. One gram of the sample is dissolved in a mixture of 50 cc. toluol and 50 cc. ethyl alcohol in a 500-cc. Erlenmeyer flask. (*Note:* Damar samples are dissolved in the toluol first, then the alcohol is added and the mixture allowed to stand 2 to 4 hours before titrating.) After standing a few minutes the solution, cloudy in the case of damar resins, is titrated with a 0.1 *N* solution of alcoholic potassium hydroxide, using phenolphthalein as an indicator. Blank determinations are run at the same time. The acid value is reported as the number of milligrams of potassium hydroxide required per gram of resin.

Determination of Indirect Acid Number. To the mixture obtained in the determination of the direct acid number is added 5 to 10 cc. excess 0.1 *N* potassium hydroxide. The flask is stoppered and allowed to stand at room temperature overnight. The mixture is then titrated back with aqueous 0.1 *N* sulfuric acid. The indirect acid value, like the direct, is calculated as milligrams potassium hydroxide per gram of resin. Blank determinations are run each time.

For dark-colored resins (particularly run resins) the end point of the titration is frequently so masked that an accurate determination becomes quite difficult. With this type of resin, rapid and satisfactory determinations can be performed by following a procedure originally developed for synthetic resins.

Determination of the Direct Acid Number of Dark Resins. Five grams of resin is dissolved in 110 cc. of a neutralized benzene-alcohol mixture (75 benzene to 35 alcohol). 25 cc. of a saturated salt solution and 10 g. of salt (sodium chloride) are added to the solution before titrating with 0.5 *N* potassium hydroxide solution. Phenolphthalein is used as the indicator.

By this method, titration is done on a two-phase medium consisting of an upper solvent layer and a lower aqueous layer. The color bodies which would ordinarily mask the end point remain in the solvent layer, while the indicator color change occurs in the aqueous layer. The end point consequently is sharp and clear. The sharpness of the separation is improved by using a salt solution rather than water alone. To maintain the saturated condition of the solution, solid salt is added to take care of the water added or formed during titration.

Determination of Saponification Number. One gram of resin is dissolved in a mixture of 25 cc. toluol and 25 cc. ethyl alcohol in a 300-cc. flask. Ten

cubic centimeters of a 0.5 N solution of potassium hydroxide in ethyl alcohol is added with a pipet. The flask is fitted with a reflux condenser and the contents boiled on a steam bath for 45 minutes. Phenolphthalein indicator is added and the liquid titrated with a standard 0.3 N aqueous solution of sulfuric acid. A blank determination is run with each set of samples. The saponification number is reported as the milligrams of potassium hydroxide per gram of resin.

Iodine Value. The Hübl method has been employed by the authors in their determinations of this value.

Determination of Iodine Number. Twenty-five grams of iodine is dissolved in 500 cc. of 95 per cent ethyl alcohol. Thirty grams of mercuric chloride is dissolved in 500 cc. of 95 per cent ethyl alcohol. The iodine solution is prepared by mixing these two solutions and allowing to stand for 12 to 24 hours. A 0.2-g. sample is dissolved in 10 cc. of pure carbon tetrachloride in a 500-cc. flask. Twenty-five cubic centimeters of the iodine solution is run in from a pipet and the flask stoppered and allowed to stand in the dark overnight. Fifteen cubic centimeters of a 10 per cent aqueous solution of potassium iodide is then added, the liquid well shaken, and diluted with 250 cc. of water. The excess of free iodine is titrated with a standard solution of sodium thiosulfate. A few drops of starch solution is used as the indicator.

The sodium thiosulfate solution is prepared by dissolving 24 g. of the crystallized salt in 1,000 cc. of water, and standardizing in the following manner: 3.8657 g. of potassium dichromate is dissolved in 1,000 cc. of water. Twenty cubic centimeters of this solution is added to 10 cc. of a 10 per cent potassium iodide solution and 5 cc. of hydrochloric acid. Since each cubic centimeter of the dichromate solution liberates exactly 0.01 g. iodine, altogether 0.2 g. iodine will be liberated. This mixture is then titrated with the thiosulfate solution and the equivalence of the latter is calculated in terms of iodine. The iodine number is reported as centigrams of iodine absorbed per gram of resin. A blank determination must be run with each set of samples.

Varnish Tests. For detailed methods of varnish testing, reference should be made to Gardner[4] and the standards of the American Society for Testing Materials.[5]

Cold Water Test. Resistance to cold water is tested by coating a 3- by 5-in. tin plate panel with one application of varnish and half immersing in distilled water at room temperature for four days.

Boiling Water Test. The panel is prepared as above, but is immersed for only 1 hour in boiling distilled water.

[4] H. A. Gardner, "Physical and Chemical Examination of Paints, Varnishes and Lacquers," ninth edition, pp. 350-62. Institute of Paint and Varnish Research, Washington, D. C., 1939.

[5] "A.S.T.M. Standards," Part II, D154-38, D358-38, D479-38T, American Society for Testing Materials, Philadelphia, Pa., 1939.

Boiling 5 per Cent Soap Solution. The panel is also prepared as above and immersed for only 1 hour in a boiling 5 per cent Ivory soap solution.

Gloss. Relative gloss was determined by examining the reflected image of a standard optician's eye-testing chart and noting the finest line of type which could be read under standard conditions. A chart having reversed letters was prepared by photographing the original on film and enlarging to the original size. In this manner the reflected image appears in regular type. The letters in line 1 were $3\frac{1}{4}$ in. and those in line 11 were 5/32 in. high. The chart was mounted at eye level opposite a window giving clear diffused light, with the varnished panel placed 5 ft. in front of the chart and slightly to one side. The panels used in this test had a baked undercoat of flat (dull) enamel.

Color and Viscosity. These are determined by the use of the Gardner Color Scale and the Gardner-Holdt Bubble Viscosimeter.

Hardness. Relative hardness may be found by the use of lead pencils of different hardnesses. A set of Venus pencils from "H" to "9H," pointed in a sharpener, are needed. The increasing numbers indicate increasing hardness. The hardness is found by pressing a pencil of suitable hardness in a perpendicular direction against a varnished metal panel. If the point crumbles, a harder pencil is tried until one is found that will just pierce the film. Piercing is confirmed by dragging the point a short distance through the film, exposing the metal beneath. The "H" number of the softest pencil that will pierce the film without breaking is taken as the hardness number. Pencils are repointed after each use. Hardness may also be determined by the Sward Hardness Rocker.

Flexibility and Adhesion. The varnish is poured on a 3- by 5-in. tin plate panel and allowed to dry. When dry, the panel is bent on a rod of 2-mm. radius and the relative flexibility and adhesion judged from the appearance of the film at the bend.

Gas-Proofness. Gas-proofness may be determined by the Bureau of Standards method for interior varnishes. In this method, panels which have been dried for one-fifth, two-fifths, three-fifths, and four-fifths of the time required to set to touch are placed in a bell jar with a lighted kerosene lamp which is allowed to burn itself out (due to the consumption of all the available oxygen). If the resultant fouled atmosphere causes any trace of crystallization or frosting of the varnish film on any panel, the varnish is listed as not gas-proof.

Non-Volatile Content. A portion of the varnish is placed in a stoppered weighing bottle and weighed. A sample of about 1.5 g. is transferred to a previously weighed, flat-bottomed dish of about 3 in. in diameter. A Petri dish or a friction-top can cover is satisfactory. The weighing bottle, together

with its remaining content of varnish, is then reweighed and the loss in weight taken as the sample weight. The sample is dried in an electric oven at 105 to 110°C., cooled, and weighed. The gain in weight of the dish represents the solids in the varnish and is reported as per cent non-volatile matter.

Kauri Reduction Test. *Preparation of Run Kauri.* Pale kauri No. 1, ground to about pea size, is heated in a closed container fitted with a water-cooled condenser. The distillate is collected in a tared receiver on a balance until condensate equal to 25 per cent by weight of resin is obtained. The run resin is then poured into a pan and permitted to cool.

The authors have found that the length of time required to run the kauri has a considerable effect on the type of run resin obtained. Therefore, the 25 per cent distillate collection is not the prime requisite for obtaining properly processed kauri. The operation should take approximately 1½ hours to perform and should produce a dark, brittle resin. Longer processing periods tend to yield softer resins. In one experiment, in which the running took 5 hours, a soft product resulted which was utterly unfit for its intended purpose.

Preparation of Kauri Turpentine Solution. The run kauri is broken up into small pieces (or finely ground) and placed in a tared container with twice its weight of freshly distilled turpentine, using only that portion distilling between the limits of 135 and 170°C. The resin can be dissolved either by heating or by cold cutting in a closed container. Any solvent lost during heating is replaced after the solution has cooled.

Determination of Kauri Reduction Number. To perform this test the non-volatile content of the varnish must be known, or determined if lacking. To 100 g. of the varnish is added an amount of kauri-turpentine solution equivalent in weight to a percentage of the non-volatile matter present in the varnish. For instance, if the varnish has a non-volatile content of 50 per cent, the amount of solution added will be expressed as a percentage of 50 g. If 50 g. of solution is added, the reduction will be 100 per cent; if 75 g. is added, the reduction will be 150 per cent, etc.

The varnish and solution are mixed thoroughly in closed bottles. A film of the varnish thus reduced is then flowed onto a clean panel of bright tin plate (No. 31 gage, 3 in. by 5 in.), permitted to stand for 1 hour in a nearly vertical position, and baked in a horizontal position in an oven at 95 to 100°C. for 5 hours. After this baking period it is removed and cooled to room temperature (preferably 25°C.) for ½ hour. The actual bending test is performed by placing the cooled panel, with the varnished side uppermost, over a ⅛-in. rod and rapidly bending the panel double. The bent portion is examined for cracking or flaking and the slightest indication of either of these means a failure.

If a failure is noted, the amount of kauri-turpentine solution used is reduced until the baked panel can be bent without film failure.

In determining kauri reduction numbers, a series of reductions is prepared at one time. If the approximate range is known, increments of 10 per cent are used. If no reasonable guess can be made as to the range, it is wiser to use larger increments and cover the entire range.

The preparation of many panels in one operation does not take much longer than the preparation of only a few and it is good policy to prepare a sufficient number at one time. A check within 10 per cent is acceptable, i.e., if duplicates are run and the failure occurs at 150 per cent once, and at 160 per cent the second time, the value is taken as the lower one—150 per cent.

A balance accurate to 0.1 g. is satisfactory when running kauri reduction tests.

When the kauri reduction test was adopted, slow-drying varnishes were the prevailing type. In order to ensure thorough drying with this varnish it was necessary to bake the test panel for 5 hours. For the newer 4-hour varnishes, it is thought that a 2- or 3-hour bake would be sufficient.[6]

The temperature at which the bending test is conducted affects the result. It has been found that by cooling the test panel to 0°C. before bending, the varnish film fails at a reduction approximately 25 per cent lower than when tested at room temperature.

The time of cooling should have no effect upon the reduction value within a reasonable limit.

The bending operation should be performed quickly. If done slowly, the film has time to adjust itself to the strain and will give a higher reduction value.

A wide viscosity difference between two varnishes yields relative results of questionable accuracy, for in the preparation of the panels the solution is flowed on and allowed to drain in a vertical position. A heavy varnish will deposit a thicker film than does a lighter varnish and the thicker film will fail before the thin film under the same bending stress.

Kauri-Butanol Test. This is a test in which a natural resin solution (kauri-butanol) is used in rating the solvencies of varnish thinners. Essentially, it is a measure of the volume of thinner which can be added to a kauri-butanol solution without causing turbidity.

The solution is prepared as follows:

One hundred parts of clean kauri resin (bush kauri is usually used) is dissolved in 500 parts of butanol. The mixture is then settled, filtered, or centrifuged to remove insoluble matter. The clarified solution is standardized using toluol, *n*-heptane, or primary reference mineral spirits[7] to give respective end points of 105, 25.8, and 40 cc. The solution may be adjusted to these figures by adding or evaporating butanol, or by mixing solutions of different resin contents. The standardization procedure has been studied by numerous investigators.[8]

[6] H. A. Gardner, "Physical and Chemical Examination of Paints, Varnishes and Lacquers," ninth edition, p. 355 (1939).

[7] Produced by the Atlantic Refining Company.

[8] *Am. Paint Varnish Mfrs. Assoc., Sci. Sect. Circ. 313,* 390 (1927); E. Fauser, *ibid., Circ. 291,* 275 (1926); *ibid., Circ. 318,* 492 (1927); S. R. Kiehl, *ibid., Circ. 319,* 595 (1927); *ibid., Circ. 378,* 145 (1931); J. R. Stewart, *ibid., Circ. 378,* 143 (1931); L. C. Beard, V. L. Shipp, and W. E. Spelshouse, *Ind. Eng. Chem., Anal. Ed.,* **5**, 307

Twenty grams of standardized kauri-butanol solution is weighed into a 250-cc. Erlenmeyer flask and brought to a temperature of 25°C. The flask is then placed on a printed sheet of paper (10-point type) and solvent added from a buret at a fairly rapid rate until a permanent turbidity has formed. Further solvent is added drop by drop until the type appears blurred and illegible when viewed through the flask containing the solution. The volume of solvent expressed in cubic centimeters necessary to cause illegibility is reported as the kauri-butanol value of the solvent. Alternate modes of expression may be as "solvent power," relative to benzene at 100 per cent or in terms of a toluol-heptane ratio possessing equal solvency.

On determination of various properties of the natural resins, Alexander[9] gave refractive indices; Harrison[10] testing methods for hardness, comparative fusibility, and loss on running; Gettens[11] the measurement of the moisture permeability of protective coatings containing natural resins; Leppert[12] a procedure for the determination of acid number of copals by the use of terpineol; Mahadevan[13] the X-ray spectra; Coburn[14] a procedure for the acid value of dark-colored resins; Stock[15] the microscopic examination of a number of little-known forest samples.

(1933); E. L. Baldeschweiler, W. J. Troeller, and M. D. Morgan, *ibid.*, 7, 374 (1935).

[9] A. E. Alexander, *Am. Mineral.*, 21, 199 (1936).

[10] A. W. C. Harrison, *Paint, Varnish Production Mgr.*, 7, No. 4, 25f. (1932).

[11] *Tech. Studies Field Fine Arts*, 1, 63-8 (1932).

[12] Z. Leppert, *Przemysl Chem.*, 15, 1-5 (1931).

[13] C. Mahadevan, *Indian J. Physics*, 5, 345-57 (1930).

[14] H. H. Coburn, *Ind. Eng. Chem., Anal. Ed.*, 2, 181 (1930).

[15] E. Stock, *Farben-Ztg.*, 32, 1967-8 (1927).

APPENDIX

MULLER, "Resins and Odoriferous Balsams," *Deut. Parfüm.-Ztg.,* **10**, 191-4 (1924).

J. SCHEIBER, "Natural and Artificial Resins," *Farbe u. Lack,* **31**, No. 7, 76; No. 8, 87; No. 9, 99; No. 10, 113 (1926).

RASSER, "Natural and Artificial Varnish Resins," *Kunststoffe,* **17**, 127-9, 160-1, 183-5 (1927).

J. DUBOURG, "Commercial Applications of Natural Resins," *Tech. Moderne,* **20**, 95-8 (1928).

A. F. SUTER, "Varnish Resins In The Far East," *Oil Colour Trades J.,* **74**, No. 1561, 777-8 (1928).

A. F. SUTER, "East Indian Copals and Damars," *J. Roy. Soc. Arts,* **77**, 577-98 (1929).

C. VAN DE KOPPEL, "The Principal Dutch Indian Resins, Gum Copal and Gum Damar," *Verfkroniek,* **2**, No. 11, 11-5 (1929).

T. H. BARRY, "Natural Resins as a Base for Synthetic Resins," *Paint Manuf.,* **2**, 215-17, 254-6 (1932).

FOURMAN, "Gums and Resins," *Drug and Cosmetic Ind.,* **33**, 228, 268 (1933).

A. J. GIBSON, "Natural Resins," *Chemistry & Industry,* 1934, pp. 989-90.

A. F. SUTER, "Natural vs. Synthetic Resins in the Paint and Varnish Industry," *Oil Colour Trades J.,* **85**, 606-9 (1934).

T. H. BARRY, "Future of Natural Resins," *Paint Manuf.,* **5**, 374-6 (1935).

H. H. NELSON, "Natural Varnish Gums," *Drugs, Oils Paints,* **50**, 242-50, 282-4 (1935).

W. STEFANOWSKI and Z. KRACZKIEWICZ, "Natural Resins," *Przemysl Chem.,* **19**, 152-3 (1935).

T. H. BARRY, "The Future of Natural Resins," *Paint Tech.,* **1**, 93-7, 131-5, 172-4, 213-16 (1936).

BRANDENBINGER, "Relations Between Artificial and Natural Resins," *Kunststoffe,* **26**, 25-7 (1936).

C. L. MANTELL, "Natural Gums and Resins as Chemical Raw Materials," *Chem. Ind.,* **38**, 577-81 (1936).

W. KRUMBHAAR, "Gums and Resins 'Down Under'," *Paint Manuf.,* **7**, 389 (1937).

T. H. BARRY, "Research on the Natural Resins," *Ind. Chemist,* **14**, 319-22 (1938).

H. S. LILLEY, "Natural and Synthetic Resins," *Paint Varnish Production Mgr.,* **18**, 206-11 (1938).

C. L. MANTELL, "Resin Economics—Synthetic and Natural," *Am. Paint J.,* Nov. 28, 1938.

C. L. MANTELL and A. SKETT, "Studies in Natural Resin Technology VIII," *Official Digest, Fed. Paint Varnish Prod. Clubs,* April, 1938.

C. L. MANTELL, A. SKETT, J. H. HOLZBERGER, R. W. ALLAN, and C. W. KOPF, "Studies in Natural Resin Technology IX," *Official Digest, Fed. Paint Varnish Prod. Clubs,* September, 1938.

A. Skett, "Recent Developments in Natural Resin Technology," *Am. Paint J.*, Jan. 24, 1938.

C. L. Mantell, A. Skett, J. H. Holzberger, R. W. Allan, and C. W. Kopf, "Studies in Natural Resin Technology X," *Official Digest, Fed. Paint Varnish Prod. Clubs,* February, 1939.

Many studies of resin samples have appeared in the literature. A few examples will be given: sambas copal,[1] Siamese damars,[2] Malayan damar,[3] damar temak,[4] Malayan damars,[5] animé,[6] Malayan varnish resins, particularly saraya, hitam or senegal, daging, kepong, kelulot, siput, minyak, and dragon's blood,[7] damar penak,[8] Papuan damar,[9] and Malayan damar penak.[10]

[1] E. Stock, *Farben-Ztg.*, **31**, 1578 (1926); **39**, 628 (1934).

[2] T. H. Barry, *Paint Varnish Prod. Mgr.*, 7, No. 2, 14, 16 (1932).

[3] E. Stock, *Farben-Ztg.*, **37**, 446-8 (1931).

[4] T. H. Barry, *J. Oil Colour Chem. Assoc.*, **14**, 204-9 (1931).

[5] T. H. Barry, *J. Oil Colour Chem. Assoc.*, **8**, 125-6, 204-6 (1925); *ibid.*, **11**, 203-18 (1928).

[6] Kunz-Krause, *Pharm. Ztg.*, 72, 1124-5, 1142-3 (1927).

[7] T. H. Barry, *J. Roy. Soc. Arts,* **76**, 106-28 (1927).

[8] *Bull. Imp. Inst.*, 22, 28-31 (1924); Blair and Byron, *Malayan Forest Rec.*, **3**, 1-12 (1926).

[9] *Bull. Imp. Inst.*, 22, 26-8 (1924).

[10] E. Cubitt, *J. Oil Colour Chem. Assoc.*, 7, 186-93 (1924).

TABLE CXLIV

Native Designations of Natural Resins*

Name	Place of Origin	Type	Present Day Classification
A			
Acaroid, *see* Accroides			
Accra copal	Liberia, Nigeria, and Gold Coast, West Africa	Fossil copal	Similar to Congo copal
Accroides, red	Australia and Tasmania		Accroides
Accroides, yellow	Australia and Tasmania		Accroides
Akra copal, *see* Accra copal			
Almaciga	Philippine Islands	Alcohol-soluble copal	Philippine Manila
Angola copal, red	Angola, West Africa	Fossil copal	Similar to Congo copal
Angola copal, white	Angola, West Africa	Fossil copal	Similar to Congo copal
Animé		Fossil copal	A term used to designate a resin from the East Coast of Africa
Animi, *see* Animé			
Ashanti copal	Gold Coast, West Africa	Fossil copal	Congo
Austral damar, *see* Kauri			
Australasian damar, *see* Kauri			
Australian copal, *see* Kauri			
Australian sandarac, *see* Sandarac			
B			
Baka			A native name for Congo copal
Batavia damar	Western Java and Eastern Sumatra, Netherlands East Indies	Damar	Batavia damar
Batjan damar	The Moluccas	Damar	
Batu Batu damar	Netherlands East Indies	Damar	Batu
Beaten damar, *see* Puti damar			
Bekongo			A native name for Congo copal
Bengkong damar	Malacca, Malay States	Damar	Damar
Benguela copal, white	South Guinea, West Africa	Fossil copal	Congo copal
Benguela copal, yellow	South Guinea, West Africa	Fossil copal	Congo copal
Benin copal	Liberia, Nigeria, and Gold Coast, West Africa	Fossil copal	Congo copal
Black boy gum, *see* Accroides			
Black damar	India	Damar	Black east india
Blonde rouge inférieure damar, *see* Cochin-China damar			

* This list includes many resin names found in the literature but not in commercial use.

TABLE CXLIV (*Continued*)

Name	Place of Origin	Type	Present Day Classification
Boea copal	Netherlands East Indies	Alcohol-soluble copal	Boea copal
Boea, brown	Netherlands East Indies	Alcohol-soluble copal	Boea copal
Boea, white	Netherlands East Indies	Alcohol-soluble copal	Boea copal
Bombay copal, *see* Zanzibar copal			
Borneo copal	Borneo, Netherlands East Indies	Alcohol-soluble copal	Pontianak copal
Borneo damar	Borneo, Netherlands East Indies	Damar	Damar
Botany Bay gum, *see* Accroides			
Brauner Borneo-damar, *see* Hiroe damar			
Brauner Fluss-damar, *see* Hiroe damar			
Brauner Sumatra-damar, *see* Hiroe damar			
Brown kauri	New Zealand	Fossil copal	Kauri copal
Bush gum	New Zealand	Fossil copal	Bush kauri
Bush kauri	New Zealand	Fossil copal	Bush kauri
Caillon (gomme), *see* Kissel copal			
Calcutta copal, *see* Zanzibar copal			
Cambodian damar	Cambodia, French Indo-China	Damar	Singapore damar
Cameroon copal	Cameroon, West Africa	Fossil copal	Congo copal
Cat's Eye damar, *see* Mata Kuching damar			
Celebes damar	Celebes, Netherlands East Indies	Damar	Batavia damar
Chakasi			A native term for semi-fossil Zanzibar copal
Chalk			A soft, porous white resin found with swamp gum
Chan	Siam	Damar	Singapore damar
Chios mastic	Island of Chios		Mastic
Cochin-China damar	Cochin-China, French Indo-China	Damar	Damar
Common sandarac	Morocco and Algeria, Africa		Sandarac
Congo copal	Belgian Congo, West Africa	Fossil copal	Congo
Copal d'arbre (*see* Congo copal)			Congo from trees
Copal d'eau (*see* Congo copal)			Congo from water
Copal de forêt (*see* Congo copal)			Congo from forest
Copal de rivière (*see* Congo copal)			Congo from rivers
Copal tendre (soft copal)			
Coquille, *see* Benguela copal			
Cowrie, *see* Kauri copal			

TABLE CXLIV (*Continued*)

Name	Place of Origin	Type	Present Day Classification
D			
Daging damar	Malay States and Borneo, Netherlands East Indies	Alcohol-soluble copal	Native designation for pontianak manila
Damar mati			"Dead" damar
"Damar Minyak"			Malayan name for Manila copal
Dangi			A native name for soft Congo copal
Dead damar	Malay States	Semi-fossil	Damar
Demerara copal	South America		A South American copal
Drop sandarac	Morocco and Algeria, Africa		Sandarac
Duging damar	Malay States and Borneo, Netherlands East Indies	Damar	Damar
E			
Earth shellac, *see* Accroides			
East Indian animé, *see* Zanzibar copal			
East Indian copal, *see* Zanzibar copal			
East Indian damar	Netherlands East Indies	Damar	Batavia damar
East Indian DBB			Manila DBB
F			
Female mastic, *see* Mastic en sorte			
Fiji kauri	Fiji Islands	Fossil copal	Kauri
Fluss damar, *see* Hiroe damar			
Friable manila, *see* Manila copal			
G			
Gaboon copal	Gaboon, West Africa	Fossil copal	Congo copal
Gelker damar, *see* Hiroe damar			
Gorontalo copal		Alcohol-soluble copal	
Gold Coast copal, *see* Ashanti copal			
Grass tree gum, *see* Accroides			
Gum juniper (erroneous term for Mogador sandarac)			

TABLE CXLIV (*Continued*)

Name	Place of Origin	Type	Present Day Classification
H			
Hard Indian gum copal (old term for Manila copal)			
Harvest kauri			Kauri collected from the tree
Hiroe damar	Malay States	Damar	Pale east india
Hitam damar	Malay States	Damar	Black east india
I			
Indian damar			Damar
Indian mastic	India		Mastic
Inhambane copal	Mozambique, East Africa	Fossil copal	Congo copal
Isio			A native name for Congo copal
Itoa			A native name for Congo copal
J			
Java copal	Java, Netherlands East Indies	Fossil copal	Boea
K			
Kala damar, *see* Black damar			
Kauri copal	New Zealand	Fossil copal	Kauri copal
Kekulot damar	Malay States	Damar	Damar
Kepong damar	Malay States	Damar	Damar
Kissel copal	Africa	Fossil copal	Congo copal
Kowrie, *see* Kauri copal			
Kula damar, *see* Black damar			
Kumus damar	Malacca, Malay States	Damar	Damar
L			
Labuan copal	British Borneo	Alcohol-soluble copal	Manila copal
Lal dhuna	India	Damar	
Lindi copal.	Lindi, East Africa	Fossil copal	Congo copal
Lisbon copal, *see* Benguela copal			
Loango copal	Guinea region, West Africa	Fossil copal	Congo copal
Loba	Netherlands East Indies	Alcohol-soluble copal	Manila copal
Lowoe copal	Netherlands East Indies	Alcohol-soluble copal	Manila copal
M			
Macassar	Celebes, Netherlands East Indies	Alcohol-soluble copal	Manila copal
Madagascar copal	Madagascar	Fossil copal	Congo copal

TABLE CXLIV (*Continued*)

Name	Place of Origin	Type	Present Day Classification
Manila copal	Malay States, Netherlands East Indies, and Philippine Islands	Alcohol-soluble copal	Manila copal
Manila elemi	Philippine Islands		Elemi
Mastic	Island of Chios, South Europe, North Africa		Mastic
Mastic en sorte	Island of Chios		Mastic
Mastic in drops, *see* Mastic officinal			
Mastic officinal	Island of Chios		Mastic
Mata Kuching damar	Malay States, notably Malacca, Sumatra, Java, Netherlands East Indies	Damar	Batavia damar
Mati damar, *see* Dead damar			
Melanti damar	Kedah, Malay States	Damar	
Melengket	Celebes, Netherlands East Indies	Alcohol-soluble copal	Manila
Meranti Bunga, *see* Daging damar			
Meranti damar	Malacca, Malay States	Damar	
Merawan damar, *see* Mata Kuching damar			
Mexican elemi			Elemi
Mogador sandarac	Morocco and Algeria		Sandarac
Mombassa copal	East Africa	Fossil copal	Congo copal
Mozambique	Mozambique, East Africa	Fossil copal	Congo copal
N			
New Zealand damar, *see* Kauri			
Nigerian elemi			
North African sandarac	Morocco and Algeria		Sandarac
Nubian copal, soft, *see* Selan damar			
O			
Ogea	Gold Coast, West Africa	Fossil copal	Congo
Oriental animé	East Africa	Fossil copal	Congo copal
P			
Padang damar	Sumatra, Netherlands East Indies	Damar	Damar
Paka			A native name for Congo copal
Pale kauri	New Zealand	Fossil copal	Kauri copal
Papuan damar	Island of Papua	Damar	Black east india
Pebble gum, *see* Kissel copal			
Pedang damar, *see* Padang damar			

TABLE CXLIV (*Continued*)

Name	Place of Origin	Type	Present Day Classification
Penak damar	Malay States	Damar	Singapore damar
Penang damar	Malay States	Damar	Singapore damar
Penjaoe damar	Dutch Borneo	Damar	
Perak damar	Malacca, Malay States	Damar	
Piney resin (or gum), *see* White (Indian) damar			
Pontianak copal	Dutch Borneo	Alcohol-soluble copal	Pontianak
Pontianak damar	Dutch Borneo	Damar	Batavia damar
Puti damar	Probably obtained from Sumatra	Damar	
R			
Raja damar	Dutch Borneo	Damar	Batavia damar
Range gum, *see* Kauri copal			
Rasak damar		Damar	Pale east india Singapore
Red gum	Australia		Accroides
Resina lutea novae belgiae, *see* Accroides, yellow			
Rock damar	India, Malay States, Borneo, Burma, Indo-China, and certain Malayan islands	Damar	Damar
Rough kauri	New Zealand	Fossil copal	Kauri copal
S			
Sal damar	India and Burma	Damar	
Sambas copal	Borneo	Alcohol-soluble copal	Pontianak
Sandarac	North and South Africa, Australia		Sandarac
Sandarach, *see* Sandarac			
Sandarusi ya m'ti			Zanzibar copal obtained direct from tree
Saraya damar	Malay States	Damar	
Selan damar	Molucca and Philippine Islands, Java, and Sumatra	Damar	
Sengai damar	Malay States	Damar	Black east india
Siamese damar	Siam	Damar	Singapore damar
Sierra Leone copal	Sierra Leone, West Africa	Fossil copal	Congo copal
Singapore damar	Malay States	Damar	Singapore damar
Siput damar	Malay States	Damar	
Songyi damar	Malacca, Malay States	Damar	
Soongyi damar, *see* Songyi damar			
South African sandarac	South Africa		Sandarac
Strayah damar	Malacca, Malay States	Damar	
Succin (amber)	Prussia	Fossil copal	Amber
Sumatra damar	Sumatra, Netherlands East Indies	Damar	Singapore damar

TABLE CXLIV (*Continued*)

Name	Place of Origin	Type	Present Day Classification
Swamp gum	New Zealand	Fossil copal	Kauri copal
Sydney, *see* Kauri copal			
"Syrup copal"			The Malayan exudation of *Agathis alba* which does not harden as rapidly as the East Indian manilas
T			
Tamak damar	Malay States	Damar	
Tanganyika copal	Tanganyika, East Africa	Fossil copal	Congo copal
Tawao damar, *see* Hiroe damar			
Ternate copal	Island of Ternate, Netherlands East Indies	Alcohol-soluble copal	Manila MA
Turkish mastic	Turkey		Mastic
U			
Uganda elemi	Uganda, East Africa		Elemi
Urushi			Natural lacquer
V			
Vare			A native name for kauri copal
W			
West African elemi	West Africa		Elemi
White (Indian) damar	India	Damar	Damar (used locally)
Y			
Yacca gum, *see* Accroides			
Yang Panawng damar			The native name of a Siamese damar
Z			
Zambas copal, *see* Sambas copal			
Zanzibar copal	Zanzibar, East Africa	Fossil copal	Congo copal

TABLE CXLV. TABLE OF PROPERTIES

	Formula	Mol. Wt.	Boiling Range		Flash Point °F.
			Initial B.P. °C.	End Point °C.	
Ketones					
Acetone	CH_3COCH_3	58.05	55	57	0
Methyl acetone	48% acetone—28% Me acetate—24% MeOH	...	54	70	23
Methyl ethyl ketone	$CH_3COC_2H_5$	72.06	77	82	34
Diethyl ketone	$C_2H_5COC_2H_5$	86.08	100	104	59
Methyl propyl ketone	$CH_3COC_3H_7$	86.08	101	107	60
Hexone (methyl isobutyl ketone)	$(CH_3)_2CHCH_2COCH_3$	100.09	112	118	74
Methyl *n*-butyl ketone	$CH_3COC_4H_9$	100.09	114	137	95
Mesityl oxide	$(CH_3)_2C{:}CHCOCH_3$	98.08	117	139	90
Diacetone alcohol	$(CH_3)_2C(OH)CH_2COCH_3$	116.09	153	160	135
Dipropyl ketone	$C_3H_7COC_3H_7$	114.11	138	144	120
Methyl *n*-amyl ketone	$CH_3COC_5H_{11}$	114.11	147	153	115
Diisobutyl ketone	$(CH_3)_2CHCH_2COCH_2CH(CH_3)_2$	142.14	164	169	145
Methyl *n*-hexyl ketone	$CH_3COC_6H_{13}$	128.12	169	173	160
Cyclohexanone	$(CH_2)_5CO$	98.08	130	173	145
Methylcyclohexanone	$(CH_2)_4CH(CH_3) : CO$	112.09	114	173	145
Acetonylacetone	$CH_3COCH_2CH_2COCH_3$	114.08	188	193	190
Phorone	$(CH_3)_2 : C : CHCOCH : C : (CH_3)_2$	138.11	114	198	180
Polyethers					
Diethyl Cellosolve	$C_2H_5OCH_2CH_2OC_2H_5$	118.11	119	125	90
Diethyl Carbitol	$C_2H_5OCH_2CH_2OCH_2CH_2OC_2H_5$	162.14	181	189	170
Esters					
Methyl acetate	CH_3COOCH_3	74.05	53	55	5
Ethyl acetate	$CH_3COOC_2H_5$	88.06	70	80	35
Isopropyl acetate	$CH_3COOCH(CH_3)_2$	102.08	84	94	35
Isopropyl acetate	$CH_3COOCH(CH_3)_2$	102.08	82	90	45
Ethyl propionate	$CH_3CH_2COOC_2H_5$	102.08	90	118	70
sec-Butyl acetate	$CH_3COOCH(CH_3)(C_2H_5)$	116.09	105	127	88
Isobutyl acetate	$CH_3COOCH_2CH(CH_3)_2$	116.09	114	118	88
n-Butyl acetate	$CH_3COOC_4H_9$	116.09	119	127	88
Ethyl butyrate	$CH_3CH_2CH_2COOC_2H_5$	116.09	107	131	85
sec-Amyl acetate	$CH_3COOCH(CH_3)(C_3H_7)$	130.11	121	144	111
Amyl acetate (mixed isomers)	$CH_3COOC_5H_{11}$	130.11	127	155	111
Butyl butyrate	$CH_3CH_2CH_2COOC_4H_9$	144.12	152	170	128
n-Butyl propionate	$CH_3CH_2COOC_4H_9$	130.11	124	171	105
Methyl amyl acetate	$CH_3COOCH(CH_3)CH_2CH(CH_3)_2$	144.12	140	147	113
Hexyl (2-ethyl butyl) acetate	$CH_3COOCH_2CH(C_2H_5)CH_2CH_3$	144.12	157	164	135
sec-Hexyl acetate	$CH_3COOCH(CH_3)(C_4H_9)$	144.12	129	158	110
Ethyl lactate	$CH_3CH(OH)COOC_2H_5$	118.08	119	176	140
Octyl (2-ethyl, hexyl) acetate	$CH_3COOCH_2CH(C_2H_5)C_4H_9$	172.16	195	203	180
Cyclohexanyl acetate	$CH_3COOCH : (CH_2)_5$	142.11	165	193	165
Isopropyl lactate	$CH_3CH(OH)COOCH(CH_3)_2$	132.09	149	167	130
Butyl lactate	$CH_3CH(OH)COOC_4H_9$	146.11	145	230	176
Glycol diacetate	$CH_3COOCH_2CH_2OOCCH_3$	146.08	184	191	205
Diglycol diacetate	$CH_3COOCH_2CH_2OCH_2CH_2OOCCH_3$	190.11	238	251	290
Diethyl carbonate	$(C_2H_5)_2CO_3$	118.08	87	128	85
3-Methoxy butyl acetate	$CH_3OCH(CH_3)CH_2CH_2OOCCH_3$	146.11	135	173	170
Methyl Cellosolve acetate	$CH_3OCH_2CH_2OOCCH_3$	118.08	143	145	132
Cellosolve acetate	$C_2H_5OCH_2CH_2OOCCH_3$	132.09	145	166	122
Butyl Cellosolve acetate	$C_4H_9OCH_2CH_2OOCCH_3$	160.12	188	192	180
Methyl Carbitol acetate	$CH_3OCH_2CH_2OCH_2CH_2OOCCH_3$	162.11	203	212	180
Carbitol acetate	$C_2H_5OCH_2CH_2OCH_2CH_2OOCCH_3$	176.12	211	220	225
Butyl Carbitol acetate	$C_4H_9OCH_2CH_2OCH_2CH_2OOCCH_3$	204.16	236	249	260

* Reprinted from *Industrial and Engineering Chemistry*, **27**, No. 10, 1169–79 (1935).

of Commonly Used Solvents*

Vapor Pressure at 30°C. Mm. Hg	Sp. Gr. at 20°C.	Wt./gal. at 20°C. lb.	Refractive Index at 20°C.	Expansion Coefficient 10–30°C.	Purity Commercial Product, %	Dilution Ratio				Solubility by Wt. at 20°C.	
						Toluene	Petroleum naphtha	Xylene	Mineral spirits	In water	Water in
277	0.793	6.60	1.3591	0.00134	99	4.5	0.7	...	...	∞	∞
...	0.831	6.92	...	0.00138	Mixt.	4.7	0.7	...	...	∞	∞
119	0.809	6.73	1.3791	0.00128	99	4.3	0.9	...	...	25.6	11.8
46	0.815	6.78	1.3927	0.00113	99	3.0	0.7	...	...	4.3	2.1
48	0.810	6.74	1.3895	0.00111	99	4.0	1.0	...	...	0.54	3.34
25	0.802	6.67	1.3959	0.00112	99	3.6	1.0	...	...	1.91	2.81
17	0.818	6.80	1.4024	0.00099	87	3.9	1.1	...	...	0.22	2.14
<10	0.855	7.12	1.4439	0.00108	86	3.8	0.9	...	...	2.89	2.85
2	0.936	7.79	1.4204	0.00094	99	...	...	2.3	0.3	∞	∞
9	0.816	6.79	1.4072	0.00107	99	3.1	0.9	2.7	0.8	0.43	0.87
7	0.818	6.81	1.4110	0.00103	98	3.9	1.2	3.6	1.1	0.4	1.4
4	0.808	6.72	...	0.00102	95	...	...	1.5	0.6	v.s.s.	v.s.s.
3	0.820	6.82	1.4161	0.00092	96	3.6	0.9	...	...	0.09	0.6
7	0.946	7.87	1.4524	0.00091	67	...	...	4.8	1.0	0.13	8.68
4	0.921	7.67	...	0.00085	74	...	...	4.5	1.0	0.15	3.04
<2	0.973	8.10	1.449	0.00093	95	...	...	1.8	imm.	∞	∞
<1	Crystals	...	1.4998	...	...	...	...	2.2	0.7	...	...
22	0.849	7.07	...	0.00120	95	...	...	0.4	0.2	2.76	4.48
1	0.909	7.56	...	0.00106	99	...	...	1.4	0.5	∞	∞
263	0.908	7.55	1.3619	0.00134	82	2.9	0.9	...	...	∞	∞
121	0.886	7.37	1.3727	0.00134	85	3.3	1.1	...	...	6.92	11.01
74	0.870	7.23	1.3770	0.00132	95	2.7	1.1	...	...	2.58	2.86
...	0.857	7.13	...	0.00119	85	3.0	1.2	...	...	2.78	5.58
43	0.891	7.41	1.3844	0.00125	96	2.1	0.8	...	...	1.92	1.22
29	0.858	7.14	1.389	0.00118	82	2.2	1.2	...	...	0.62	1.65
27	0.870	7.24	1.3997	0.00119	96	2.7	1.1	...	...	0.67	1.64
16	0.876	7.29	1.3951	0.00117	90	2.9	1.3	2.7	1.3	0.43	1.86
22	0.880	7.32	1.3932	0.00116	99	1.9	0.7	...	...	0.49	0.75
10	0.862	7.18	...	0.00113	92	2.2	1.0	2.0	0.6	0.19	0.88
9	0.862	7.17	...	0.00104	84	2.1	1.2	...	...	0.17	1.15
4	0.874	7.27	1.4049	0.00107	99	1.6	0.7	...	...	0.05	0.43
7	0.874	7.27	...	0.00106	99	2.4	1.2	2.2	0.7	0.15	0.80
2	0.857	7.13	1.4008	0.00109	95	1.7	1.0	1.6	0.8	0.08	0.89
5	0.876	7.29	1.4103	0.00106	91	...	...	2.0	1.1	0.06	0.75
10	0.861	7.16	...	0.00104	98	...	...	1.8	0.8	v.s.s.	0.68
5	1.034	8.60	1.4118	0.00098	98	6.3	0.7	...	...	∞	∞
<1	0.873	7.27	1.4300	0.00099	99	...	...	1.4	1.0	v.s.s.	0.39
7	0.963	8.01	...	0.00095	79	2.5	1.4	...	...	0.16	1.42
5	0.988	8.22	...	0.00101	99	5.0	1.2	...	...	∞	∞
5	0.980	8.16	...	0.00099	97	5.2	2.7	5.1	2.1	4.0	14.5
<1	1.107	9.21	1.415	0.00102	99	...	...	1.4	imm.	21.3	21.2
<1	1.116	9.29	...	0.00095	99	...	...	1.3	imm.	∞	∞
17	0.957	7.96	1.3852	0.00113	91	1.1	0.5	...	...	1.88	2.60
3	0.956	8.37	...	0.00100	99	...	...	2.1	0.9	6.46	3.72
6	1.005	8.37	1.4025	0.00110	99	2.3	0.6	1.9	0.4	∞	∞
3	0.974	8.10	1.4030	0.00111	96	2.5	0.9	2.3	0.7	24.7	9.4
<1	0.943	7.85	...	0.00104	99	...	...	1.9	1.0	0.9	1.9
<1	1.040	8.65	...	0.00099	99	...	...	1.7	0.3	∞	∞
<1	1.011	8.41	1.4230	0.00101	97	...	...	1.9	0.6	∞	∞
<1	0.987	8.21	...	0.00094	99	...	...	1.8	0.6	1.6	3.4

For details of testing procedure and conditions refer to original article.

TABLE CXLV

	Formula	Mol. Wt.	Boiling Range		Flash Point °F.
			Initial B.P. °C.	End Point °C.	
Ether-Alcohols					
Methyl Cellosolve	$CH_3OCH_2CH_2OH$	76.06	121	126	105
Cellosolve	$C_2H_5OCH_2CH_2OH$	90.08	133	137	111
Isopropyl Cellosolve	$(CH_3)_2CHOCH_2CH_2OH$	104.09	140	143	125
Butyl Cellosolve	$C_4H_9OCH_2CH_2OH$	118.11	163	172	165
Methyl Carbitol	$CH_3OCH_2CH_2OCH_2CH_2OH$	120.09	190	194	200
Carbitol	$C_2H_5OCH_2CH_2OCH_2CH_2OH$	134.11	189	203	205
Butyl Carbitol	$C_4H_9OCH_2CH_2OCH_2CH_2OH$	162.14	220	231	230
Benzyl Cellosolve	$C_6H_5CH_2OCH_2CH_2OH$	152.09	254	258	265
Alcohols					
Methanol (anhydrous)	CH_3OH	32.03	64	66	52
Ethanol (anhydrous)	C_2H_5OH	46.05	77	79	65
Isopropanol (anhydrous)	$(CH_3)_2CHOH$	60.06	82	83	67
sec-Butanol	$CH_3CH_2CHOHCH_3$	74.08	96	103	88
Isobutanol	$(CH_3)_2CH_2CHOH$	74.08	107	111	111
n-Butanol	C_4H_9OH	74.08	116	119	111
sec-Amyl alcohol	$(CH_3CH_2)_2CHOH$	88.09	117	124	110
Amyl alcohol (mixed isomers)	$C_5H_{11}OH$	88.09	121	139	111
Methyl amyl alcohol	$(CH_3)_2CHCH_2CH(CH_3)OH$	102.11	131	132	114
Hexyl (2-ethyl butyl) alcohol	$CH_3CH_2CH(C_2H_5)CH_2OH$	102.11	144	156	145
Octyl (2-ethyl hexyl) alcohol	$C_4H_9CH(C_2H_5)CH_2OH$	130.14	182	201	178
Cyclohexanol	$C_6H_{11}OH$	100.09	150	182	170
Benzyl alcohol	$C_6H_5CH_2OH$	108.06	199	204	212
Hydrocarbons					
Benzene	C_6H_6	78.05	78	81	<5.5
Toluene	$C_6H_5CH_3$	92.06	109	111	44
Xylene	$C_6H_4(CH_3)_2$	106.08	127	159	80
Hi-Flash naphtha		...	149	193	115
Petroleum naphtha		...	96	129	31
V.M. & P. naphtha		...	168	210	120
Mineral spirits		...	152	207	140
Cyclohexane	C_6H_{12}	84.09	80	83	<6.5
Tetrahydronaphthalene	$C_{10}H_{12}$	132.09	196	217	180
Decahydronaphthalene	$C_{10}H_{18}$	138.14	186	194	145
Solvesso No. 1		...	94	139	45
Solvesso No. 2		...	134	185	110
Solvesso No. 3		...	179	214	155
Safe-T-Esso		...	157	217	145
Chlorinated compounds					
Ethylene dichloride	$ClCH_2CH_2Cl$	98.95	82	84	70
Monochlorobenzene	C_6H_5Cl	112.50	130	134	95
Orthodichlorobenzene	$C_6H_4Cl_2$	146.95	177	180	175
Dichloroethyl ether	$ClCH_2CH_2OCH_2CH_2Cl$	142.98	172	178	185
Naval stores solvents					
Gum spirits of turpentine		...	154	201	110
Steam distilled turpentine		...	155	173	115
Dipentene	$CH_3(C_6H_8)C:(CH_2)CH_3$	136.13	172	200	145
Hercosol		...	176	262	150
Pine Oil		...	99	226	185
Heavy pine oil		...	211	219	200
Fenchone	$(CH_3)_3C_6H_7C:O$	152.13	190	210	160
Furane derivatives					
Furfural	$(C_4H_3O)CHO$	96.03	110	169	145
Furfuryl acetate	$CH_3COOCH_2(C_4H_3O)$	140.06	180	186	185
Furfuryl alcohol	$(C_4H_3O)CH_2OH$	98.05	152	220	175
Tetrahydrofurfuryl alcohol	$(C_4H_7O)CH_2OH$	102.08	119	204	180

* Reprinted from *Industrial and Engineering Chemistry*, 27, No. 10, 1169–79 (1935).

(*Continued*)*

Vapor Pressure at 30°C. Mm. Hg	Sp. Gr. at 20°C.	Wt./gal. at 20°C. lb.	Refractive Index at 20°C.	Expansion Coefficient 10–30°C.	Purity Commercial Product, %	Dilution Ratio				Solubility by Wt. at 20°C.	
						Toluene	Petroleum naphtha	Xylene	Mineral spirits	In water	Water in
<2	0.966	8.04	1.4028	0.00094	99	4.0	imm.	2.9	imm.	∞	∞
7	0.931	7.75	1.4080	0.00097	99	4.9	1.1	4.3	0.7	∞	∞
8	0.906	7.53	...	0.00093	97	4.3	1.6	3.8	1.3	∞	∞
2	0.902	7.50	1.4190	0.00087	99	3.5	2.3	3.2	1.9	∞	∞
<1	1.035	8.62	1.4244	0.00087	...	...	...	1.0	imm.	∞	∞
<1	1.027	8.55	...	0.00082	...	...	...	1.2	imm.	∞	∞
<1	0.955	7.95	1.4290	0.00087	96	...	...	4.2	1.2	∞	∞
<1	1.070	8.90	...	0.00076	99	...	...	3.0	imm.	0.4	18.1
160	0.793	6.60	1.329	0.00118	99	2.5	0.3	...	...	∞	∞
78	0.791	6.58	1.361	0.00108	99	...	...	...	...	∞	∞
60	0.786	6.54	1.3776	0.00107	99	...	...	...	...	∞	∞
26	0.808	6.72	1.397	0.00091	99	...	...	...	...	12.5	44.1
17	0.803	6.68	1.396	0.00095	99	...	...	...	...	10	16.9
11	0.811	6.75	1.3974	0.00094	99	...	...	...	...	8.0	19.5
12	0.810	6.74	...	0.00088	95	...	...	...	...	0.13	9.87
...	0.814	6.77	...	0.00093	99	...	...	...	...	0.09	8.98
6	0.807	6.72	1.4087	0.00100	99	...	...	...	...	1.73	6.37
4	0.833	6.93	1.4229	0.00089	99	...	...	...	...	0.63	4.56
<1	0.834	6.94	1.4300	0.00088	99	...	...	...	...	0.06	2.48
2	0.951	7.92	1.4656	0.00077	94	...	...	...	...	0.13	11.78
<1	1.047	8.71	1.5399	0.00073	99	...	...	...	...	0.08	8.37
118	0.878	7.31	1.5014	0.00124	...	...	...	...	...	0.19	insol.
26	0.866	7.21	1.4962	0.00107	...	...	...	...	...	0.05	insol.
11	0.862	7.17	...	0.00099	...	...	...	...	...	v.s.s.	insol.
...	0.860	7.16	...	0.00094	...	...	...	...	...	v.s.s.	insol.
...	0.735	6.11	...	0.00115	...	...	...	...	...	v.s.s.	insol.
...	0.763	6.36	...	0.00098	...	...	...	...	...	v.s.s.	insol.
...	0.769	6.40	...	0.00098	...	...	...	...	...	v.s.s.	insol.
121	0.779	6.48	1.4273	0.00108	...	...	...	...	...	v.s.s.	insol.
<1	0.972	8.09	1.5461	0.00083	...	...	...	...	...	v.s.s.	insol.
2	0.885	7.37	...	0.00088	...	...	...	...	...	v.s.s.	insol.
...	0.796	6.62	...	0.00108	...	...	...	...	...	v.s.s.	insol.
...	0.847	7.09	...	0.00091	...	...	...	...	...	v.s.s.	insol.
...	0.877	7.29	...	0.00089	...	...	...	...	...	v.s.s.	insol.
...	0.874	7.27	...	0.00089	...	...	...	...	...	v.s.s.	insol.
94	1.256	10.45	1.444	0.00116	99	...	...	...	...	0.87	0.16
15	1.108	9.22	1.525	0.00092	99	...	...	...	...	v.s.s.	insol.
3	1.308	10.88	1.549	0.00083	99	...	...	...	...	v.s.s.	insol.
2	1.222	10.17	1.4570	0.00097	99	...	...	...	...	1.02	0.1
...	0.868	7.22	...	0.00090	...	...	...	...	...	v.s.s.	insol.
...	0.857	7.13	...	0.00089	...	...	...	...	...	v.s.s.	insol.
2	0.853	7.10	1.473	0.00086	...	...	...	...	...	v.s.s.	insol.
...	0.912	7.59	...	0.00083	...	0.4	0.1	...	...	v.s.s.	insol.
...	0.925–0.935	7.7	...	0.00066	...	...	...	...	...	v.s.s.	1.7
...	0.937–0.942	7.8	...	0.00085	...	...	...	...	...	v.s.s.	2.4
2	0.948	7.89	1.4647	0.00088	...	...	...	2.9	0.8	0.2	0.5
5	1.159	9.64	1.5261	0.00087	98	...	...	1.6	imm.	8.3	4.8
1	1.119	8.42	1.4627	0.00094	99	...	...	1.3	imm.	v.s.s.	insol.
2	1.137	9.46	1.4852	0.00077	98	...	...	1.5	imm.	∞	∞
<1	1.051	8.74	...	0.00074	99	...	...	2.6	imm.	∞	∞

For details of testing procedure and conditions refer to original article.

TABLE CXLVI. CHARACTERISTICS OF VARIOUS PETROLEUM NAPHTHAS

	Trade Name	Manufacturer	Type of Solvent	Specific Gravity	Distillation Range			
					Initial		Final	
					°C.	°F.	°C.	°F.
1	D. C. naphtha	Standard Oil Co. of Ohio	Paraffin	0.748	91	195	168	335
2	Varnolene	Standard Oil Co. of Ohio	Paraffin	0.782	149	300	207	405
3	Kerosene	Standard Oil Co. of Ohio	Paraffin	0.809	177	350	277	530
4	Torch oil	Standard Oil Co. of Ohio	Paraffin	0.864	266	510	393	740
5	Solvent naphtha No. 54	Standard Oil Co. of N. J.	Paraffin	0.72	77	170	121	250
6	Solvent naphtha No. 55	Standard Oil Co. of N. J.	Paraffin	0.735	93	200	135	275
7	V. M. P. naphtha	Standard Oil Co. of N. J.	Paraffin	0.771	99	210	157	315
8	Varsol No. 2	Standard Oil Co. of N. J.	Paraffin	0.79	152	305	202	395
9	Solvesso No. 1	Standard Oil Co. of N. J.	High aromatic	0.795	93	200	141	285
10	Solvesso No. 2	Standard Oil Co. of N. J.	High aromatic	0.852	129	265	182	360
11	Solvesso No. 3	Standard Oil Co. of N. J.	High aromatic	0.884	188	370	218	425
12	Solvesso No. 4	Standard Oil Co. of N. J.	High aromatic	0.930	205	401	241	466
13	Petrobenzol	Anderson-Prichard Oil Co.	Paraffin with some naphthenes	0.699	60	140	92	198
14	Troluoil	Anderson-Prichard Oil Co.	Paraffin with some naphthenes	0.733	93	200	120	248
15	Apcothinner	Anderson-Prichard Oil Co.	Paraffin with some naphthenes	0.758	117	243	141	285
16	Apco 125	Anderson-Prichard Oil Co.	Paraffin with some naphthenes	0.784	163	325	198	388
17	Apco B-75	Anderson-Prichard Oil Co.	Paraffin with some naphthenes	0.798	174	345	264	508
18	Sunoco spirits	Sun Oil Co.	High naphthenic	0.801	149	300	207	405
19	Special Sunoco spirits	Sun Oil Co.	Paraffin	0.784	149	300	207	405
20	Sinclair rubber solvent	Sinclair Oil Co.	Paraffin	0.708	48	118	142	287
21	Sinclair naphthol	Sinclair Oil Co.	Paraffin	0.735	87	189	138	281
22	Sinclair VMP naphtha	Sinclair Oil Co.	Paraffin	0.745	97	206	166	330
23	Sinclair solvent	Sinclair Oil Co.	Paraffin	0.783	153	307	204	399
24	Sinclair odorless insecticide base	Sinclair Oil Co.	Paraffin	0.790	178	353	257	495
25	Shell lacquer diluent "A"	Shell Oil Co. of Calif.	Mixed paraffin and naphthene	0.734	69	156	132	270
26	Shell lacquer diluent "B"	Shell Oil Co. of Calif.	Mixed paraffin and naphthene	0.781	133	271	169	337
27	Shell lacquer diluent "C"	Shell Oil Co. of Calif.	Mixed paraffin and naphthene	0.746	98	208	148	298
28	Shell TS-1 solvent	Shell Oil Co. of Calif.	Mixed paraffin and naphthene	0.786	159	318	194	382
29	Shell TS-11 solvent	Shell Oil Co. of Calif.	High aromatic	0.819	112	234	172	342
30	Shell TS-16 solvent	Shell Oil Co. of Calif.	High aromatic	0.831	142	288	189	372
31	Shell TS-28 solvent	Shell Oil Co. of Calif.	High aromatic	0.851	160	320	203	398
32	Shell rubber solvent "A"	Shell Oil Co. of Calif.	Mixed paraffin and naphthene	0.731	78	172	110	230
33	Shell odorless kerosene	Shell Oil Co. of Calif.	Mixed paraffin and naphthene	0.804	185	365	253	488
34	Shell P & V thinner	Shell Oil Co. of Calif.	Mixed paraffin, naphthene, and aromatic	0.811	158	316	203	398
35	Shell paint base spirits	Shell Oil Co. of Calif.	Mixed paraffin, naphthene, and aromatic	0.804	157	315	205	401
36	Shell white spirits	Shell Oil Co. of Calif.	Mixed paraffin and naphthene	0.787	153	307	180	356
37	Union solvent No. 8	Union Oil Co. of Calif.	Aromatic	0.793	97	207	133	272
38	Union solvent No. 30	Union Oil Co. of Calif.	Aromatic	0.846	140	284	181	358
39	Union solvent No. 40	Union Oil Co. of Calif.	Aromatic	0.871	189	372	211	412
40	Socal thinner No. 355L	Standard Oil Co. of Calif.	Aromatic	0.849	159	318	198	388
41	Standard thinner No. 200	Standard Oil Co. of Calif.	Paraffin	0.741	74	166	122	252
42	Standard thinner No. 250	Standard Oil Co. of Calif.	Paraffin	0.753	92	198	143	290
43	Standard thinner No. 300	Standard Oil Co. of Calif.	Paraffin	0.790	119	246	203	397
44	Standard thinner No. 350	Standard Oil Co. of Calif.	Paraffin	0.821	155	312	209	408
45	Standard thinner No. 410	Standard Oil Co. of Calif.	Paraffin	0.829	182	360	236	458

TABLE CXLVII

Temperature Conversion Table

°C		°F	°C		°F	°C		°F	°C		°F	°C		°F
−73.3	**−100**	−148	1.67	**35**	95.0	26.7	**80**	176.0	104.4	**220**	428	229.5	**445**	833
−67.8	**−90**	−130	2.22	**36**	96.8	27.2	**81**	177.8	107.2	**225**	437	232.2	**450**	842
−62.2	**−80**	−112	2.78	**37**	98.6	27.8	**82**	179.6	110.0	**230**	446	235.0	**455**	851
−56.7	**−70**	−94	3.33	**38**	100.4	28.3	**83**	181.4	112.8	**235**	455	237.8	**460**	860
−51.1	**−60**	−76	3.89	**39**	102.2	28.9	**84**	183.2	115.6	**240**	464	240.5	**465**	869
−45.6	**−50**	−58	4.44	**40**	104.0	29.4	**85**	185.0	118.3	**245**	473	243.3	**470**	878
−40.0	**−40**	−40	5.00	**41**	105.8	30.0	**86**	186.8	121.1	**250**	482	248.9	**480**	896
−34.4	**−30**	−22	5.56	**42**	107.6	30.6	**87**	188.6	123.9	**255**	491	254.4	**490**	914
−28.9	**−20**	−4	6.11	**43**	109.4	31.1	**88**	190.4	126.7	**260**	500	260	**500**	932
−23.3	**−10**	14	6.67	**44**	111.2	31.7	**89**	192.2	129.4	**265**	509	268.6	**510**	950
−17.8	**0**	32	7.22	**45**	113.0	32.2	**90**	194.0	132.2	**270**	518	271.1	**520**	968
−17.2	**1**	33.8	7.78	**46**	114.8	32.8	**91**	195.8	135.0	**275**	527	276.7	**530**	986
−16.7	**2**	35.6	8.33	**47**	116.6	33.3	**92**	197.6	137.8	**280**	536	282.2	**540**	1004
−16.1	**3**	37.4	8.89	**48**	118.4	33.9	**93**	199.4	140.6	**285**	545	287.8	**550**	1022
−15.6	**4**	39.2	9.44	**49**	120.2	34.4	**94**	201.2	143.3	**290**	554	293.3	**560**	1040
−15.0	**5**	41.0	10.0	**50**	122.0	35.0	**95**	203.0	146.1	**295**	563	298.9	**570**	1058
−14.4	**6**	42.8	10.6	**51**	123.8	35.6	**96**	204.8	148.9	**300**	572	304.4	**580**	1076
−13.9	**7**	44.6	11.1	**52**	125.6	36.1	**97**	206.6	151.7	**305**	581	310	**590**	1094
−13.3	**8**	46.4	11.7	**53**	127.4	36.7	**98**	208.4	154.4	**310**	590	315.6	**600**	1112
−12.8	**9**	48.2	12.2	**54**	129.2	37.2	**99**	210.2	157.2	**315**	599	321.1	**610**	1130
−12.2	**10**	50.0	12.8	**55**	131.0	37.8	**100**	212.0	160.0	**320**	608	326.7	**620**	1148
−11.7	**11**	51.8	13.3	**56**	132.8	40.6	**105**	221.0	162.8	**325**	617	332.2	**630**	1166
−11.1	**12**	53.6	13.9	**57**	134.6	43.3	**110**	230	165.6	**330**	626	337.8	**640**	1184
−10.6	**13**	55.4	14.4	**58**	136.4	46.1	**115**	239	168.3	**335**	635	343.3	**650**	1202
−10.0	**14**	57.2	15.0	**59**	138.2	48.9	**120**	248	171.1	**340**	644	348.9	**660**	1220
−9.44	**15**	59.0	15.6	**60**	140.0	51.7	**125**	257	173.9	**345**	653	354.4	**670**	1238
−8.89	**16**	60.8	16.1	**61**	141.8	54.4	**130**	266	176.7	**350**	662	360	**680**	1256
−8.33	**17**	62.6	16.7	**62**	143.6	57.2	**135**	275	179.4	**355**	671	365.6	**690**	1274
−7.78	**18**	64.4	17.2	**63**	145.4	60.0	**140**	284	182.2	**360**	680	371.1	**700**	1292
−7.22	**19**	66.2	17.8	**64**	147.2	62.8	**145**	293	185.0	**365**	689	376.7	**710**	1310
−6.67	**20**	68.0	18.3	**65**	149.0	65.6	**150**	302	187.8	**370**	698	382.2	**720**	1328
−6.11	**21**	69.8	18.9	**66**	150.8	68.3	**155**	311	190.6	**375**	707	387.8	**730**	1346
−5.56	**22**	71.6	19.4	**67**	152.6	71.1	**160**	320	193.4	**380**	716	393.3	**740**	1364
−5.00	**23**	73.4	20.0	**68**	154.4	73.9	**165**	329	196.1	**385**	725	398.9	**750**	1382
−4.44	**24**	75.2	20.6	**69**	156.2	76.7	**170**	338	198.9	**390**	734	404.4	**760**	1400
−3.89	**25**	77.0	21.1	**70**	158.0	79.4	**175**	347	201.7	**395**	743	410	**770**	1418
−3.33	**26**	78.8	21.7	**71**	159.8	82.2	**180**	356	204.4	**400**	752	415.6	**780**	1436
−2.78	**27**	80.6	22.2	**72**	161.6	85.0	**185**	365	207.2	**405**	761	421.1	**790**	1454
−2.22	**28**	82.4	22.8	**73**	163.4	87.8	**190**	374	210.0	**410**	770	426.7	**800**	1472
−1.67	**29**	84.2	23.3	**74**	165.2	90.6	**195**	383	212.8	**415**	779	432.2	**810**	1490
−1.11	**30**	86.0	23.9	**75**	167.0	93.3	**200**	392	215.6	**420**	788	437.8	**820**	1508
−0.56	**31**	87.8	24.4	**76**	168.8	96.1	**205**	401	218.4	**425**	797	443.3	**830**	1526
0	**32**	89.6	25.0	**77**	170.6	98.9	**210**	410	221.1	**430**	806	448.9	**840**	1544
0.56	**33**	91.4	25.6	**78**	172.4	100.0	**212**	413.6	224.0	**435**	815	454.4	**850**	1562
1.11	**34**	93.2	26.1	**79**	174.2	101.7	**215**	419	226.7	**440**	824			

Note: The numbers in bold-face type refer to the temperature either in degrees Centigrade or Fahrenheit which it is desired to convert into the other scale. *Example:* If converting from Fahrenheit degrees to Centigrade degrees, the equivalent temperature will be found in the left column, and when converting from degrees Centigrade to degrees Fahrenheit, the equivalent temperature will be found in the column on the right.

NAME INDEX

SUBJECT INDEX